

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**SYNTHESIS OF CuInSe₂/ZnS QUANTUM DOTS AND INVESTIGATION OF
DYE ADSORPTION PROPERTIES FOR WASTE TREATMENT**



M.Sc. THESIS

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Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**CuInSe₂/ZnS KUANTUM NOKTALARININ SENTEZİ VE ATIK ARITMA
İÇİN BOYA ADSORPSİYON ÖZELLİKLERİNİN ARAŞTIRILMASI**

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ABBREVIATIONS

3-MPA	: 3-Mercaptopropionic acid
a.u.	: Arbitrary Unit
cm	: Centimeter
DW	: Distilled water
FTIR	: Fourier Transform Infrared Spectroscopy
L-GSH	: L-Glutathione
M	: Molar
MB	: Methylene Blue
mg	: Milligram
ml	: Milliliter
mmol	: Millimole
MO	: Methyl Orange
NAC	: N-acetyl-L-cysteine
nm	: Nanometer
pH	: Potential of Hydrogen
PL	: Photoluminescence Spectroscopy
QDs	: Quantum Dots
RB	: Rhodamine B
rpm	: Revolutions per minute
UV-Vis	: Ultraviolet-visible Spectroscopy
XRD	: X-Ray Diffraction Analysis



SYMBOLS

%	: Percentage
°C	: Degree Celsius
cm⁻¹	: Wavenumber
λ	: Wavelength
μ	: Micro
θ	: Angle





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SYNTHESIS OF CuInSe₂/ZnS QUANTUM DOTS AND INVESTIGATION OF DYE ADSORPTION PROPERTIES FOR WASTE TREATMENT

SUMMARY

In recent years, rapidly increasing industrial growth, specifically in the paper and textile sectors, has led to a significant environmental threat to water resources. In addition, organic dyes released as a result of these industrial activities and frequently found in water sources carry a serious risk to both the environment and human health. Research on the removal of organic dyes is gaining importance due to their harmful effects on human health, such as the risk of cancer as well as their toxicity and potential to remain in the environment for long periods. Compared to various traditional methods for removing the dyes, the adsorption method emerges as a promising approach in terms of efficiency, as it is both more cost-effective and offers easy application.

In this thesis, the potential of quantum dots for adsorption studies against organic dyes was investigated. Quantum dots, one of the most recent developments in the field of nanotechnology, are widely used in many areas due to their outstanding optical and photophysical properties. In this study, their dye removal performance was examined through the adsorption studies conducted and the underlying mechanism, particularly due to their surface advantage.

In the experimental part, CuInSe₂/ZnS core/shell quantum dots which containing no heavy metals such as cadmium and lead were synthesized and capped with three different ligands: L-glutathione, N-acetyl-L-cysteine, and 3-mercaptopropionic acid. The synthesis of core/shell CuInSe₂/ZnS quantum dots was carried out in one pot, in aqueous medium, under reflux and nitrogen gas for a total reaction time of 1.5 hours. In this process, syntheses were also conducted by doubling the amounts of copper nitrate hemi-pentahydrate as copper source and indium acetate as indium source, while keeping all other parameters constant, to examine the effect of metal stoichiometry on the structure and optical properties.

In the second stage, the structural properties of the synthesized quantum dots were characterized using XRD, FTIR, and Raman spectroscopy. The XRD spectrum confirmed the crystal structure, and the analysis of the structure verified the formation of a core/shell structure and confirmed that the material is quantum dot. A common finding observed in the FTIR spectra of all synthesized quantum dots is the disappearance of thiol peaks typically seen around 2500 cm⁻¹ on all ligand surfaces. This result indicates that all three selected ligands have successfully bonded to the quantum dot via sulfur atoms.

To characterize their optical properties, the solubility of the quantum dots was also investigated in a total of seven pH solutions ranging from pH 5 to pH 11 using photoluminescence and UV spectroscopy. Since no conclusive results were obtained regarding the optimal pH at which they dissolve, they were considered unsuitable for use in pH sensor applications. However, it was clearly observed that the L-glutathione

capped CuInSe₂/ZnS QDs dissolved at pH 11. The investigation of such pH-dependent solubility provides valuable insight for adsorption studies with dyes.

Following the characterization of structural and optical properties, adsorption studies were conducted using three different dyes. These dyes were methylene blue, rhodamine B and methyl orange. After these three dyes were interacted with quantum dots, the adsorption mechanism was investigated using UV spectroscopy and FTIR methods. According to the UV results, methylene blue exhibits the best interaction with the quantum dots, and the highest removal efficiency of 99.1% was observed with N-acetyl-L-cysteine capped Cu(x2)InSe₂/ZnS QDs.

Although the primary adsorption mechanism here is explained by electrostatic interactions arising from the positive and negative charges on the surfaces of the dye and quantum dots, FTIR spectra of the adsorption products suggest that hydrogen bonding and hydrophobic interactions also play a critical role. Another important factor is the type of ligand that is used in the synthesis of QDs. For instance, since L-glutathione is a larger ligand with greater steric hindrance compared to others, L-GSH capped QDs' dye adsorption performance is lower.

Desorption experiments were conducted to investigate the potential for recovering the adsorbed dye. During this study, two different approaches were employed: a solvent based approach and a thermal based approach. In the solvent based approach, methanol was added to the quantum dots that had interacted with the dyes and analyzed via UV spectroscopy. In the thermal based approach, distilled water was added to the quantum dots adsorbing the dye, followed by a shaking in a water bath at 50°C. According to the results obtained from UV spectroscopy after the experiments, no dye recovery was observed following thermal treatment, whereas the experiments conducted with methanol, characteristic spectrum of the pristine dyes were observed, particularly for the quantum dots that had interacted with rhodamine B and methylene blue.

In summary, the potential of QDs developed for environmental applications was thoroughly investigated in adsorption and desorption processes. Analytical results and characterization results showed that the QDs were capable of adsorbing different dye molecules, showing the highest adsorption efficiency toward methylene blue.

CuInSe₂/ZnS KUANTUM NOKTALARININ SENTEZİ VE ATIK ARITMA İÇİN BOYA ADSORPSİYON ÖZELLİKLERİNİN ARAŞTIRILMASI

ÖZET

Son yıllarda özellikle kağıt ve tekstil başta olmak üzere endüstrinin çeşitli alanlarında hızla gelişen faaliyetler, su kaynakları açısından önemli bir tehdit oluşturmaktadır. Özellikle de bu endüstriyel faaliyetler sonucu açığa çıkan ve su kaynaklarında da sıkça rastlanan organik boyalar, hem çevre hem de insan sağlığı için ciddi bir risk taşımaktadır. Bu organik boyalara örnek olarak metilen mavisi, rodamin B ve metil turuncusu gibi türler verilebilir. Organik boyaların kanser riski taşımaları gibi insan sağlığına zararlı etkileriyle beraber hem doğada uzun süre kalabilmeleri hem de toksik olmaları nedeniyle giderilmeleri üzerine yapılan çalışmalar önem kazanmaktadır. Bu nedenle uygulanan çeşitli boya giderme yöntemleri bulunmaktadır. Bunlara örnek olarak ise ters osmoz, kimyasal çöktürme, koagülasyon, yüzdürme, iyon değişimi, elektrokimyasal iyileştirme ve adsorpsiyon gibi farklı yaklaşımlar gösterilebilir. Bu yöntemler arasında çöktürme ve koagülasyon gibi geleneksel metotlara kıyasla adsorpsiyon yöntemi, hem daha az maliyetli olması hem de uygulama kolaylığı sağlayarak verimlilik açısından umut vaat eden bir yöntem olarak ortaya çıkmaktadır.

Bu tez çalışmasında, organik boyalar ile adsorpsiyon çalışmaları için kuantum noktaların potansiyeli araştırılmıştır. Nanoteknoloji alanındaki en güncel gelişmelerden biri olan kuantum noktalar, üstün optik ve fotofiziksel özellikleriyle birçok alanda yaygın olarak kullanılmaktadır. Özellikle sahip oldukları yüzey avantajı sayesinde boya giderme performansları, yürütülen adsorpsiyon çalışmaları ve mekanizması üzerinden incelenmiştir.

İlk aşamada, kadmiyum ve kurşun gibi ağır metaller içermeyen daha çevre dostu kuantum nokta türünün sentezlenmesine odaklanılmıştır. Bu amaç doğrultusunda, I-III-VI grubuna ait CuInSe₂/ZnS çekirdek-kabuk yapılı kuantum noktalar sentezlenerek L-glutasyon, N-asetil-L-sistein ve 3-merkaptopropiyonik asit olmak üzere üç farklı ligantla kaplanmıştır. Kabuk yapısının eklenmesi, kuantum noktaların kararlılığını sağlamasıyla beraber, aynı zamanda ligantlarla etkileşimi ve çözünürlüğü gibi özelliklerini de etkilemektedir. Ayrıca boya adsorpsiyon çalışmaları için yüzey özelliklerinin belirleyici ve kritik bir faktör olmasından dolayı, ligantlarla kaplandıktan sonra yüzey özellikleri FTIR spektrumunda incelenmiştir.

Çekirdek/kabuk yapılı CuInSe₂/ZnS kuantum noktalarının sentezi tek kapta, su içerisinde, geri akış sağlayan kondenser ve azot gazı altında toplam 1.5 saat reaksiyon süresinde gerçekleştirilmiştir. Ana çözelti hazırlanırken pH değeri 8 olacak şekilde ayarlanıp 100°C’de reaksiyon gerçekleştirilmiştir. Bu süreçte üç farklı ligantla etkileşimin yanı sıra, metal sitokiyometrisinin yapıya ve optik özelliklere etkisini incelemek amacıyla diğer tüm parametreler sabit tutulup sadece bakır kaynağı olan bakır nitrat hemipentahidrat ve indiyum kaynağı olan indiyum asetat miktarları ayrı ayrı 2 katına çıkartılarak sentezler yapılmıştır. Sentez sonucunda üç farklı ligantla kaplı, ve farklı metal sitokiyometrilere sahip toplamda dokuz adet kuantum nokta

elde edilmiştir. elde edilmiştir. Bu kuantum noktalar reaksiyon sonunda katı halde elde edilmiş ve 2-8 °C’de buzdolabında muhafaza edilmiştir.

İkinci aşamada, elde edilen kuantum noktaların yapısal özelliklerinin karakterizasyonu XRD, FTIR ve Raman ile gerçekleştirilmiştir. XRD analizi ile kristal yapı aydınlatılarak literatürde yer alan diğer sentezlerin sonuçlarıyla kıyaslanmıştır. Bu kıyaslamalar ve yapının inceleme sonucunda da malzemenin kuantum nokta olduğu ve çekirdek/kabuk yapısının olduğu doğrulanmıştır. FTIR sonuçları ise sentez aşamasında kullanılan üç ayrı ligantın ve kuantum noktalar arasındaki bağlanma ve fonksiyonel gruplar hakkında önemli bilgiler sunmaktadır. Sentezlenen bütün kuantum noktaların FTIR spektralarında ortak olarak görülen sonuç, tüm ligant yüzeylerinde 2500 cm⁻¹ civarında görülen tiyol piklerinin, sentezlenen kuantum noktalarda gözlemlenmemesidir. Bu sonuç, seçilen üç ligantın da kuantum noktaya kükürt atomu üzerinden başarıyla bağlandığını göstermektedir.

Optik özelliklerinin karakterizasyonu için de kuantum noktaların, saf su ile 0.001 molar sodyum hidroksit ve hidroklorik asit kullanılarak hazırlanılan pH 5 değerinden 11 değerine kadar olan toplam yedi adet pH çözeltisindeki çözünürlüğü fotoluminesans ve UV spektroskopisi ile incelenmiştir. En iyi hangi pH değerinde çözüldüklerine yönelik rasyonel bir sonuç alınmadığı için pH sensörü uygulamalarında kullanımı için uygun görülmemiştir. Ancak özellikle L-glutasyon ligantı ile kaplı CuInSe₂/ZnS kuantum noktasının pH 11’de çözüldüğü net bir şekilde gözlemlenmiştir. Bu gibi pH’a bağlı çözünürlüklerin incelenmiş olması da boyalar ile yapılacak olan adsorpsiyon çalışmaları için önemli bir öngörü sunmaktadır.

Yapısal ve optik özelliklerin karakterizasyonundan sonra üçüncü aşamada, üç farklı boya ile adsorpsiyon çalışmaları yürütülmüştür. Bu boyalar katyonik yüklü metilen mavisi, ortamın pH değerine bağlı olarak değişen bir diğer katyonik boya türü olan rodamin B ve anyonik karaktere sahip metil turuncusudur. Bu üç boya dokuz farklı kuantum noktalarla etkileştirildikten sonra UV spektroskopisi ve FTIR metotlarıyla incelenerek adsorpsiyon mekanizması araştırılmıştır. UV sonuçlarına göre, kuantum noktalarla en iyi etkileşime giren metilen mavisi olup en yüksek giderim verimliliği %99.1 ile N-asetil-L-sistein ligantıyla kaplı Cu(x2)InSe₂/ZnS’dir. Ayrıca etkileşim öncesi ve sonrası çözeltilerin renk değişimleri de görsel olarak incelenmiş olup buradaki renk değişimlerinin UV sonuçlarındaki yoğunluk düşüşleriyle paralel olduğu saptanmıştır. Metilen mavisinden sonra ise kuantum noktalarla etkileşimi yüksek olan rodamin B olup anyonik karakterdeki metil turuncusunun etkileşimi diğerlerine göre daha sınırlı kalmıştır. Buradaki temel adsorpsiyon mekanizması boya ve kuantum nokta yüzeyindeki artı/eksi yüklerin varlığıyla meydana gelen elektrostatik etkileşimlerle açıklanıyor olsa da, hidrojen bağı ve hidrofobik etkileşimlerin de rolü olduğu boya sonrası yapılan FTIR analizleriyle açıklanmaktadır. Ayrıca bunlarla birlikte, kullanılan ligant türü de kritik rol oynamaktadır. Örneğin L-glutasyon diğerlerine göre daha hacimli ve sterik engele sahip bir ligant olduğu için boya adsorbe etme performansı daha düşük kalmıştır.

Adsorpsiyon çalışmalarından sonra dördüncü aşamada, adsorbe edilen boyanın geri kazanımını incelemek amacıyla desorpsiyon çalışmaları gerçekleştirildi. Bu çalışma sırasında, çözücü bazlı ve termal bazlı olmak üzere iki farklı yaklaşım benimsendi. Çözücü bazlı yaklaşımda kullanılan metanol, boyalarla etkileşime girmiş kuantum noktalara eklenerek UV spektroskopisinde analiz edildi. Termal bazlı yaklaşımda ise boyayı adsorplayan kuantum noktalara distile su eklenerek 50°C’de su banyosunda çalkalama işlemine tabi tutuldu. Deney sonrası alınan UV spektroskopisindeki

sonuçlara göre ısıtılma işlemde herhangi bir boya geri kazanımı görülmezken, metanol ile yapılan deney sonuçlarında özellikle rodamin B ve metilen mavisi ile etkileştirilmiş kuantum noktalarda saf boyanın karakteristik absorpsiyon spektrumu gözlemlendi.

Sonuç olarak çevresel iyileştirme amaçlarıyla geliştirilen ve kadmiyum gibi toksik metaller içermeyen kuantum noktalarının adsorpsiyon ve desorpsiyon süreçlerindeki potansiyeli kapsamlı bir şekilde incelendi ve diğer boyalara göre özellikle metilen mavisinin adsorpsiyonunda diğer incelenen boyalara kıyasla daha yüksek verim ve adsorpsiyon kapasitesine ulaştığını göstermiştir.





1. INTRODUCTION

1.1 Quantum Dots

Quantum dots (QDs) are nanoscale particles which are semiconducting nanocrystals typically containing 100–1,000 atoms, exhibit unique optical and electronic properties (Petryayeva et al., 2013). They are usually composed of elements from the II-VI, III-V or IV groups and, as shown in Figure 1.1, and they have attracted considerable interest among researchers in recent years due to variety of uses such as bioimaging, photovoltaics, cancer cell therapy, photoelectrons, light-emitting diode (LED) technology, and sensors (Chung et al., 2021; Kirkwood et al., 2018).

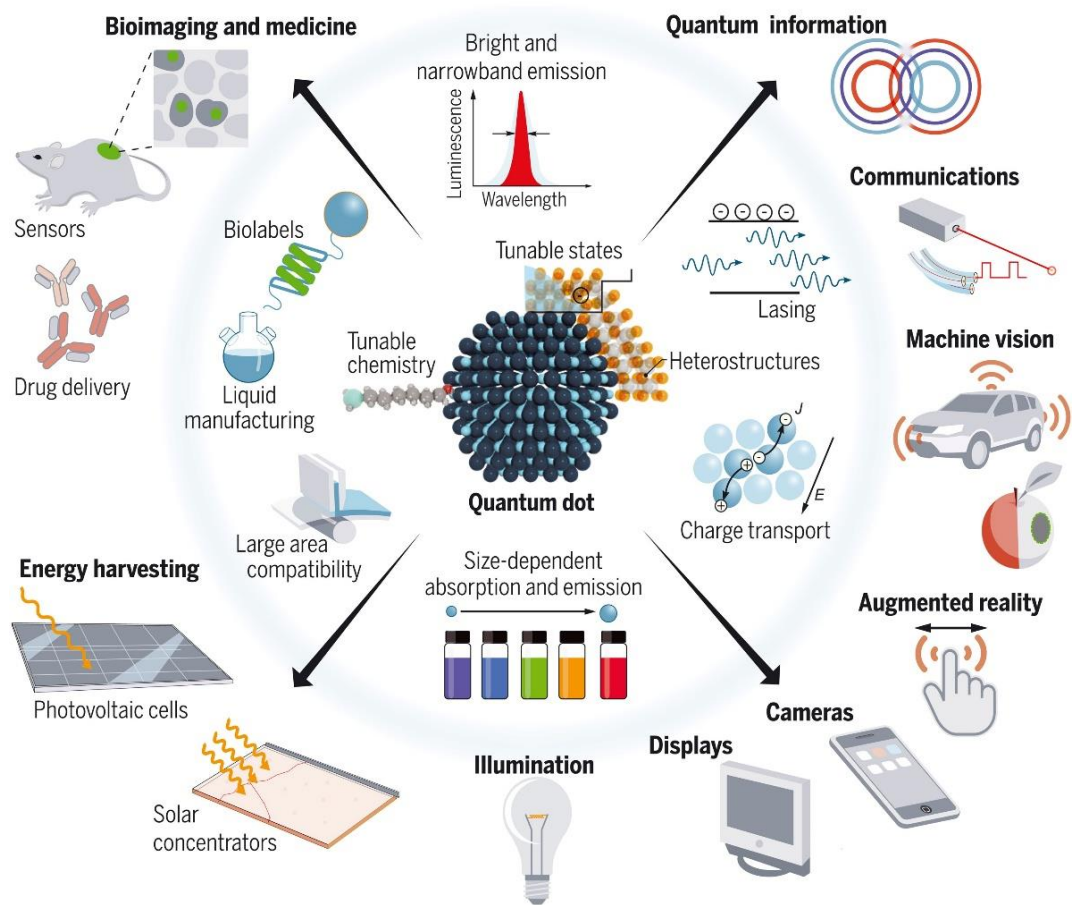


Figure 1.1 : Application areas of QDs (Talpin et.al, 2021).

QDs are basically synthesized using two models: the core or the core/shell model. In the core/shell structure, a semiconductor core consists of inorganic materials is coated with a shell, and this shell improves the physical and optical properties of the QDs (Ghasemi et al., 2009; Gidwani et al., 2021). Whereas the inorganic core determines the optical and semiconductor features of QDs, as shown in Figure 1.2 the shell structure enables the surface to be functionalized with various ligands (Reshma & Mohanan, 2018). This structure also enhances potential areas of application by providing properties such as solubility in water or another solvent.

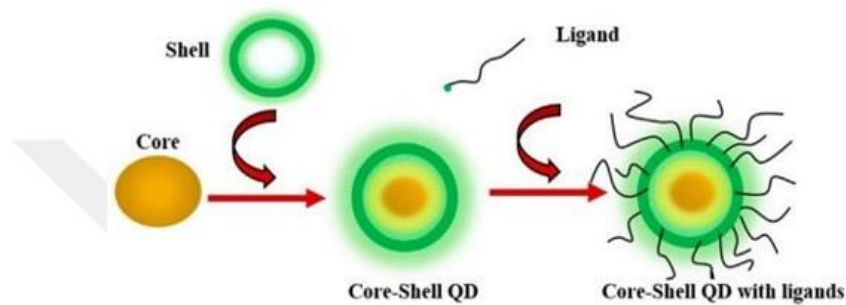


Figure 1.2 : Structure of core shell QDs with ligands (Kalsoom et.al, 2021).

1.1.1 Quantum confinement

The size dependent optical properties exhibited by QDs are explained by the quantum confinement effect, which causes a change in their energies across the bandgap (Manikandan & Lee, 2022). As shown in Figure 1.3, in the process of light absorption, where electrons move from the valence band to the conduction band to form an exciton (electron-hole pair); when the particle size falls below the Bohr radius, the energy needed to create this exciton rises, and the quantum confinement effect which is typically observed in ultra small scale nanostructures occurs (Kumar et.al, 2018; Maxwell et.al, 2019).

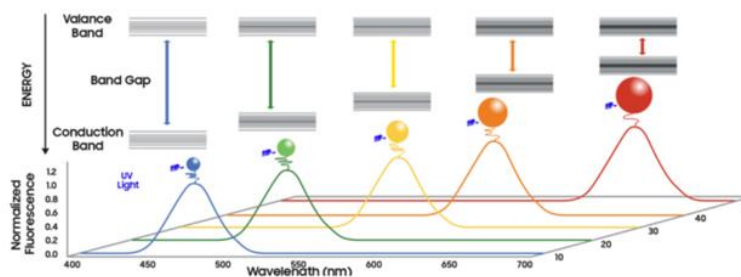


Figure 1.3 : Distinctive optical characteristics under size dependent quantum confinement effect (Maxwell et.al, 2019).

1.1.2 Types of quantum dots

QDs can be divided into different categories based on their composition, structure, size and preparation techniques. According to their composition, they can be classified as: III–V semiconductor QDs, Group IV QDs, II–VI semiconductor QDs, ternary/quaternary QDs (I–III–VI), carbon based QDs, perovskite QDs (Abid et al., 2025). For instance, III–V QDs such as InAs, InP, GaAs do not contain cadmium are being widely investigated as sustainable candidates for clinical imaging applications (Abid et al., 2025; Zhou et al., 2015). Group IV QDs (Ge,Si) also provide potential for photonic, sensor and battery applications because of their steady structures and compatibility with current silicon technology (Abid et al., 2025). Group II–VI chalcogenide QDs (CdSe, ZnS, ZnSe, CdS, CdTe) can emit light of every color thanks to their wide bandgap and high luminous efficiency; however, due to the harmful heavy metals they contain, they are currently being replaced by environmentally friendly alternatives (Abid et al., 2025). For this reason, research is being carried out on the synthesis of cadmium free QD types, such as InP, CuInS₂, CuInSe₂, and silicon or carbon based quantum dots, and their applications in a variety of industrial fields, including biophotonics and nanomedicine, as seen in Figure 1.4 (Xu et al., 2016).

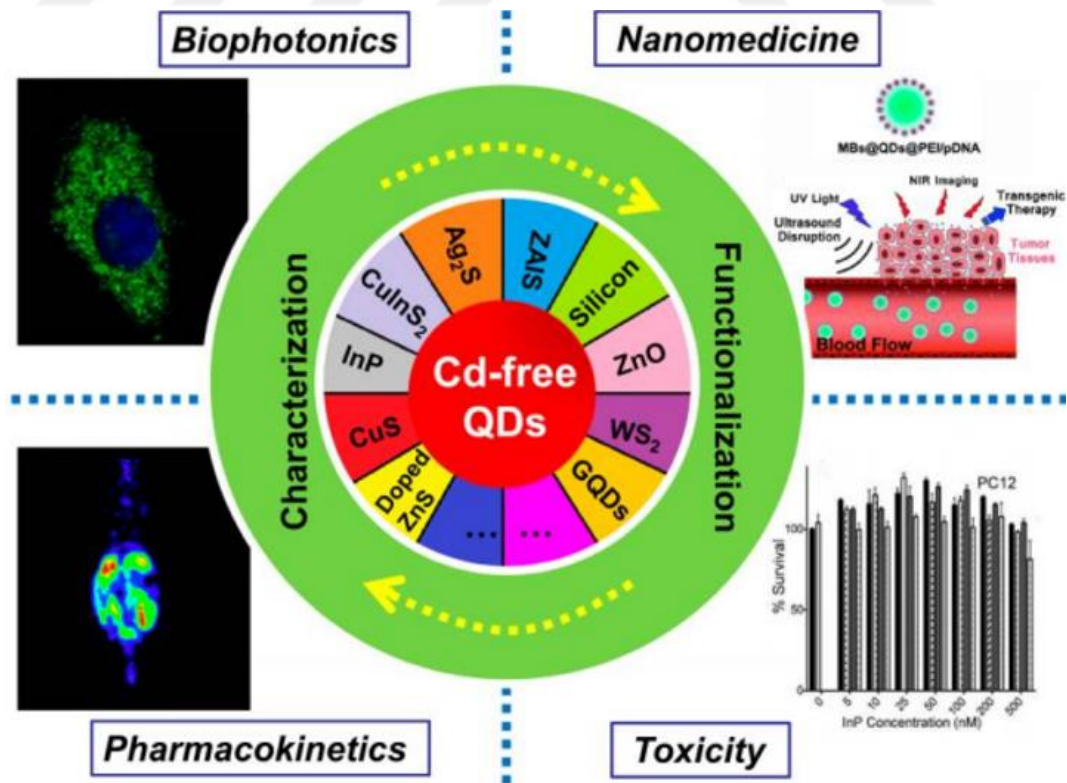


Figure 1.4 : Cadmium free QDs and application areas (Xu et al., 2016).

Group I-III-VI QDs are semiconductor materials that consist of a combination of Group I (Cu, Ag), Group III (Ga, In, Tl), and Group VI (S, Se, Te, etc.) of the periodic table, and widely studied examples include AgInSe₂, CuGaS₂, and CuInS₂, CuInSe₂ (Chen, Y. et al., 2023; Chen, T. et al., 2023; Shi et al., 2020). Compared to binary QDs, this type of QDs provides control over luminous emission by altering its chemical composition (e.g., Ag or Cu) to adjust the emitted light to the needed wavelength (Chen et al., 2023). For instance, Chuang et al. (2014) observed that during the CuInS₂ synthesis process, the emission bandgap extended and thermal stability decreased when the amount of Cu was reduced to varied ratios while maintaining the same In content. These type of QDs have also the potential to be used in fields such as solar cells, bioimaging, and white LEDs (Chen et al., 2023; Wei et al., 2021). Generally, a core-shell structure is formed by coating the system with materials like ZnS, Al₂O₃, and SiO₂ in order to remove the negative effects of changes within the crystals caused by variations in the reaction rates of different metal ions on the luminescence efficiency during the synthesis of QDs (Chen et al., 2023). CuInSe₂ QDs, which stands out in this group, extends luminescence absorption range into the near-infrared (NIR) region due to its larger Bohr radius and narrower bandgap compared to CuInS; this makes it particularly suitable for various applications, primarily in the field of optics, as shown in Figure 1.5 (Chen et al., 2024; Li et al., 2015).

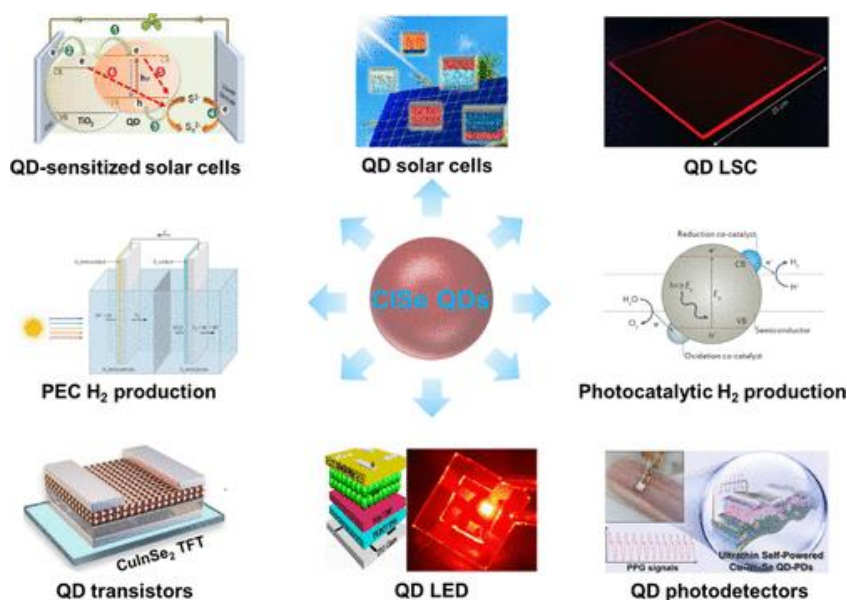


Figure 1.5 : Application areas of CuInSe₂ (Chen et al., 2024).

In this thesis, CuInSe₂/ZnS core shell QDs were synthesized by doubling the amounts of both copper and indium separately.

1.1.3 Synthesis of QDs

QDs preparation techniques can be divided into two methods: top-down and bottom-up (Zhang & Veerakumar, 2012). Hydrothermal/solvothermal and microwave-assisted techniques are the main components of the bottom-up method and the hydrothermal/solvothermal method is one of the most used approaches for QDs synthesis (Wang & Ni, 2014; Zhang et al., 2021).

1.1.3.1 Hydrothermal/solvothermal approaches

These techniques, which are conducted at high temperatures and pressures and are known as hydrothermal when water is used as solvent and solvothermal when an organic solvent is used, have been used in many research investigations in the literature because of their practical application and environmental compatibility. For instance, Agarwal et al. (2023) synthesized the nitrogen doped carbon QDs using hydrothermal method as shown in Figure 1.6.

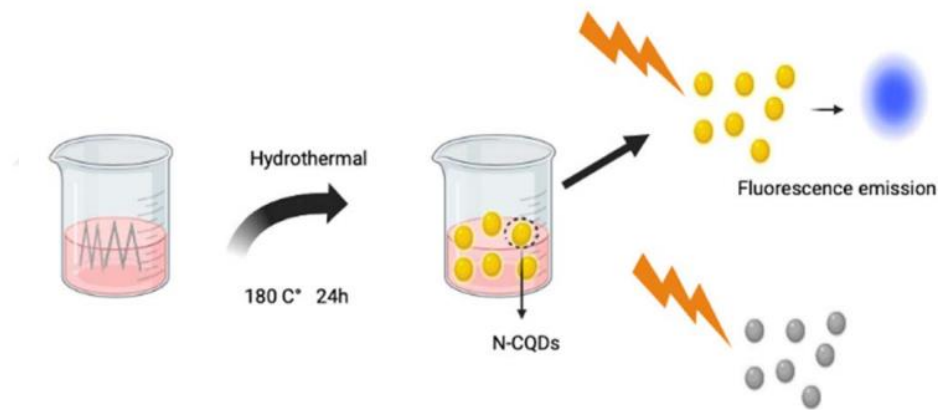


Figure 1.6 : Example of the synthesis via hydrothermal method (Agarwal et al., 2023).

According to another study of CuInSe_2 QD synthesis in the literature, the researchers also used a hydrothermal approach to generate these type of QDs (Chen et al., 2021), heating the solution to 170 celsius degree for an hour. The Figure 1.7 represents the reaction scheme.

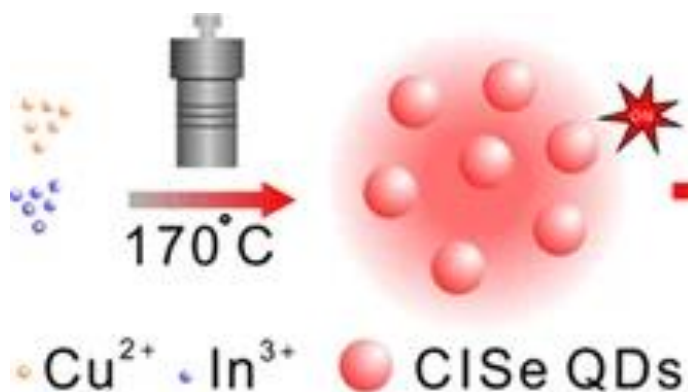


Figure 1.7 : Synthesis illustration of CuInSe_2 (Chen et al., 2021).

On the other hand, Jawhar et al. (2020) presented a different approach by synthesizing $\text{CuInS}_2/\text{ZnS}$ QDs through one pot aqueous synthesis using a glass flask instead of an autoclave. The study noted that this process was carried out in a reflux condenser at 100°C for 45 minutes. During the synthesis process, the pH of the core mixture was adjusted to 8, and all steps were completed under nitrogen gas; the resulting colloidal solution was then precipitated using acetone and extracted for analysis in solid form (Chen et al., 2021).

1.1.3.2 Microwave assisted approaches

This method uses electromagnetic waves to achieve uniform heating throughout the material, enabling the formation of nanomaterials with a narrow particle size distribution in a short time and with lower energy consumption (Gupta et al., 2018; Li et al., 2016). In Figure 1.8, schematic representation of this method is shown.

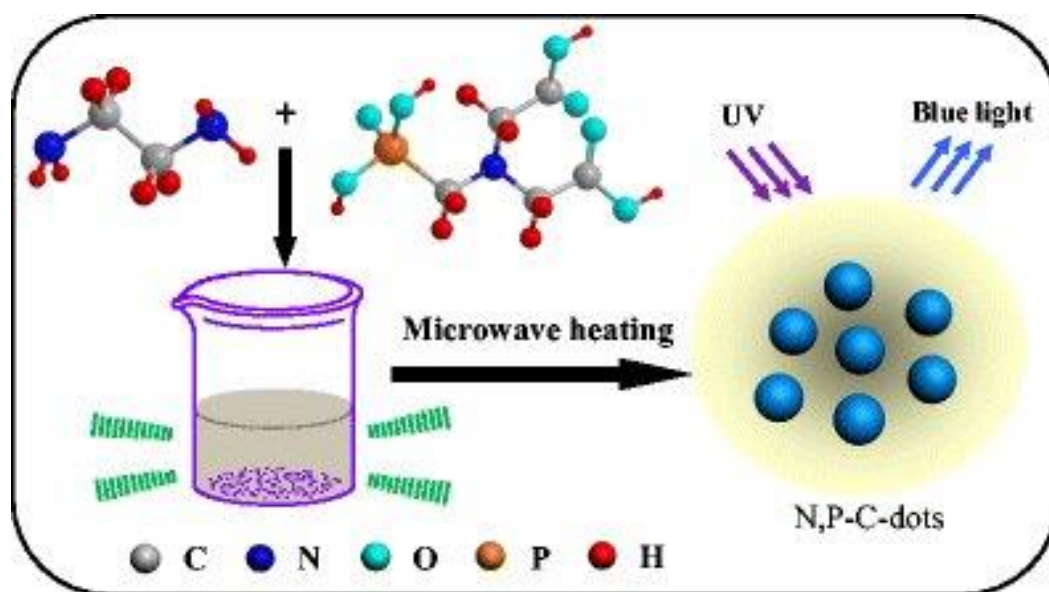


Figure 1.8 : Example of microwave-assisted synthesis route (Li et al., 2016).

1.2 Adsorption of Dyes for Waste Treatment

Technological advancements and rapid population growth have led to increased freshwater consumption, resulting in large amounts of wastewater being discharged into natural habitats (Zhang et.al, 2021). One of the main factors of polluting the environment and water is dyes which are organic compounds and mostly utilized in the paper and textile industries (Yang et al., 2021). They can be cationic, anionic, or zwitterionic, depending on their chemical structure (Heidari et al., 2019). Removing these organic dyes is essential for protecting human health because they can potentially cause negative consequences like dermatological conditions, breathing problems, and in specific cases, cancers (Aragaw & Bogale, 2021). In Figure 1.9, several dye removal techniques are shown. When all methods are compared, one of the most effective and outstanding approach for removing dye is adsorption due to its cost advantage, high efficiency, lack of reactivity to hazardous materials and simple of use (Tafese et.al, 2023).

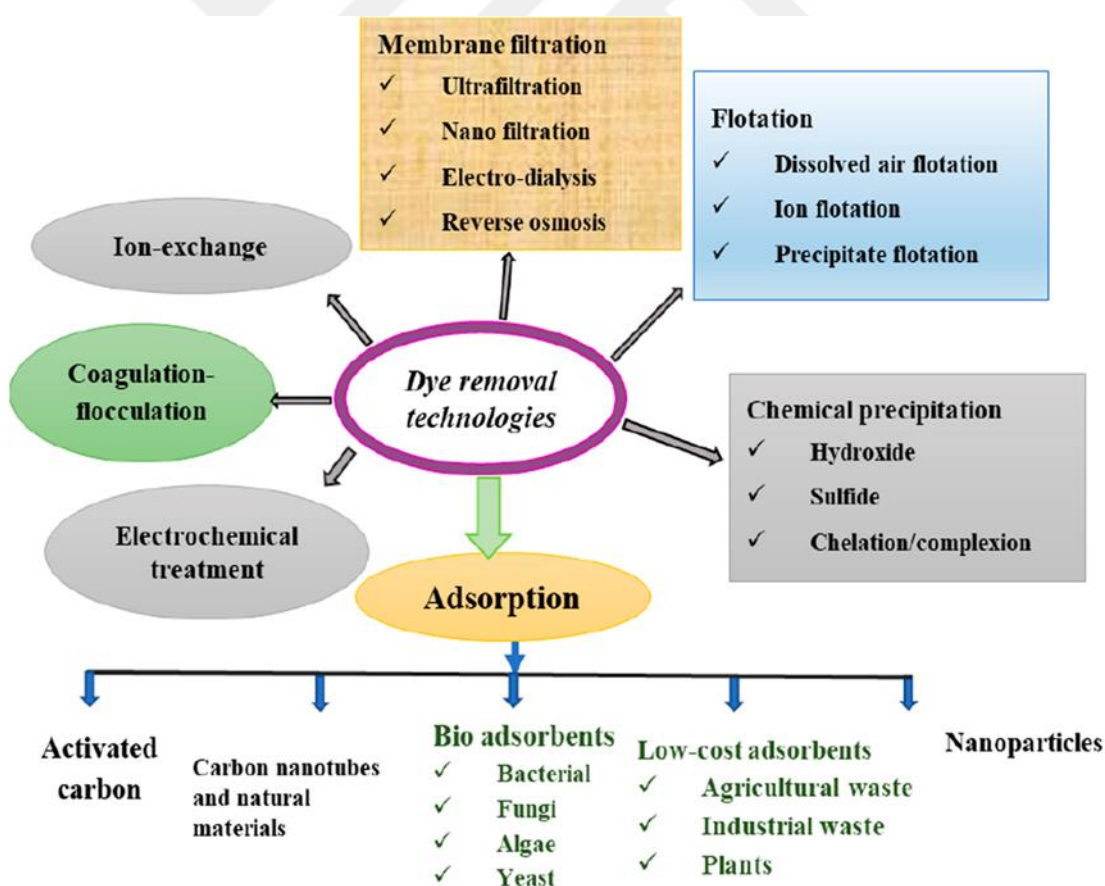


Figure 1.9 : Dye removal approaches (Aragaw & Bogale, 2021).

Compounds adhere to a solid surface in two dimensions through a process called adsorption. Seen in Figure 1.10, the adsorption mechanism is divided into two main mechanisms as chemisorption and physisorption (Agarwala & Mulky, 2023).

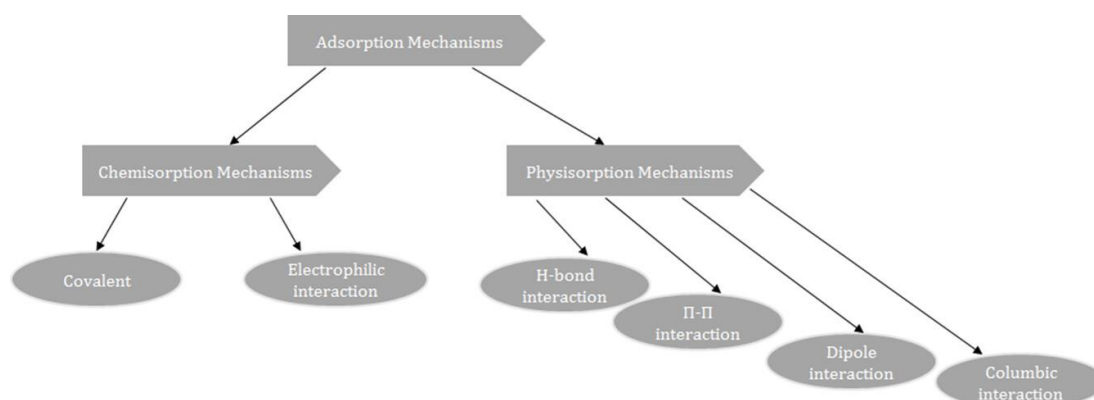


Figure 1.10 : Schematic illustration of adsorption mechanisms (Agarwala & Mulky, 2023).

For chemisorption mechanisms, strong covalent bonds occur between the adsorbent and the adsorbate which is not only less frequently observed than physical adsorption but can also be similarly challenging to break bonds (Shen et al., 2019). On the other hand, physical adsorption is a process resulting from weak intermolecular forces such as dipole-dipole forces and Van der Waals interactions (Erkey, 2011). The adsorbed materials separate from the surface more readily during the physisorption process which is called desorption, because the binding forces are not as strong as in chemical adsorption (Agarwala & Mulky, 2023). In addition, there are some main conditions such as pH, temperature, adsorbent concentration, and contact time impacting the adsorption process (Agarwala & Mulky, 2023). However, important factors like the adsorbent having a large surface area in this process, the adsorbent's desorption efficiency is also critical for its reuse (Ayawei et al., 2017).

Desorption can be considered the opposite of adsorption; it is generally the process by which a substance is released from a surface. Although the cost of some adsorbents is high, research into desorption techniques continues because these adsorbents may have the potential to be recovered for industrial use through desorption processes (Ayawei et al., 2017). A review of the literature indicates that desorption methods is generally classified under three main categories: thermal and the use of acidic or basic substances (Ong et al., 2020). When analyzing the solvents used in the studies, it is observed that chemicals such as nitric acid (HNO₃), acidic ethanol, deionized water,

acetic acid, hydrochloric acid (HCl), and a sodium hydroxide (NaOH)-ethanol mixture were employed (Agarwala & Mulky, 2023; Bilal et al., 2022; Vunain & Biswick, 2019). Tafese et al. (2024) reported that in desorption experiments following the adsorption of MB dye onto nitrogen and phosphorus doped carbon QDs, distilled water (DW) was initially tested but was found to be insufficient for effectively desorbing the dye molecules in their study. It was stated that the use of acidic ethanol as a solvent, as shown in Figure 1.11, they were able to obtain an 82% desorption efficiency after 5 cycles (Tafese et al. (2024).

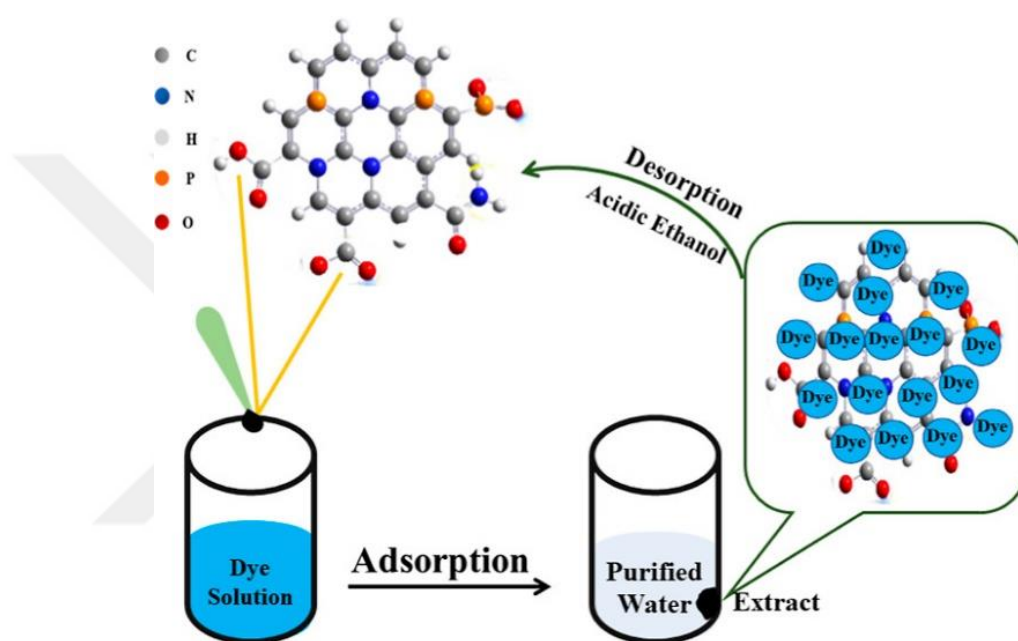


Figure 1.11 : Schematic illustration of adsorption and desorption approaches (Tafese et al., 2024).

In a different research, Agarwala and Mulky (2023) found that the bioadsorbent removed the dye with just a 5% loss of its adsorption capacity in a desorption examination using a 50% aqueous ammonia solution. Thus, these studies in the literature highlight the importance of desorption processes carried out concurrently with adsorption processes. In this thesis, three dyes with different properties were selected for use in adsorption processes involving QDs: the anionic dye methyl orange (MO), the cationic dye methylene blue (MB), and rhodamine B (RB), which exhibits cationic properties depending on pH. After interaction with QDs, desorption studies were conducted with distilled water at 50 degree celsius and methanol.

1.3 Purpose of Thesis

The primary objective of this thesis is the synthesis of environmentally friendly QDs that do not contain heavy and toxic metals, particularly cadmium and lead. In this context, I-III-VI group CuInSe₂/ZnS core/shell nanostructures were synthesized in the aqueous phase under reflux conditions. To enhance the solubility and stability of the synthesized QDs in distilled water, a core/shell structure was formed, and the particles were capped with three different ligands: 3-mercaptopropionic acid (3-MPA), L-glutathione (L-GSH), and N-acetyl-L-cysteine (NAC). Besides from all reaction parameters during the synthesis were remained constant, the amounts of copper and indium precursors in the core solutions were each doubled separately to investigate the effects of stoichiometric changes of metals in the core composition on the structural and optical properties of the QDs.

After the synthesis of QDs, the second objective is to investigate adsorption properties of QDs on various dyes. Since organic dyes are one of the main causes of water and environmental pollution, it is important to removal of these dyes for human health. For this reason, experiments were conducted to examine the potential of QDs for this purpose. In the experimental part, three different dyes MB, RB, and MO will be used as organic dyes. The interactions that may occur with these dyes were investigated using structural and optical characterization techniques, and calculate the removal efficiency values for each QD separately.

The third objective is to investigate the reusability of dyes after adsorption studies. This is also a critical factor; for example, MB has potential applications in the medical field, and its recovery is of significant importance. After the adsorption studies, desorption parts were conducted to determine whether it is possible to recover the adsorbed dye. Due to the fact that two main different regeneration approaches as solvent-based and thermal-based were studied. This will provide a comprehensive examination of the adsorption and recovery potential of cadmium free QDs developed for environmental remediation purposes.

This thesis consists of a total of four main sections. The introduction section contains information based on literature reviews regarding QDs, the targeted application areas, and adsorption and desorption processes. In the subsequent materials and methods section, all experimental procedures are described in details. In the following part, the

obtained results from applied characterization techniques and their explanations are presented. The final section will provide an overview of the results obtained.





2. MATERIALS AND METHODS

2.1 Materials

To synthesize QDs, indium (III) acetate ($\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3$, 99.9% trace metals basis, Merck), copper(II) nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, ACS reagent, 98%, Merck), citric acid monohydrate (ACS reagent grade, $\geq 99.5\%$, crystals, Merck), sodium hydroxide (NaOH, ACS reagent, $\geq 97.0\%$, pellets, Merck), N-acetyl-L-cysteine (NAC, 99.9%, Aldrich), L-glutathione reduced (L-GSH) (98.0%, Aldrich), 3-mercaptopropionic acid (3-MPA, 99.9%, Aldrich), sodium borohydride (NaBH_4 , 98.0%, Merck), selenium powder (100 mesh, 99.5%, Aldrich), thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99.0%, Merck), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%, Aldrich), acetone (ACS grade, Aldrich), ethanol (ACS grade, Aldrich), methanol (ACS grade, Aldrich), hydrochloric acid (37%, Merck) methylene blue powder, methyl orange powder, rhodamine B powder, and distilled water were used.

2.2 Synthesis of QDs

In this study, $\text{CuInSe}_2/\text{ZnS}$ QDs were synthesized in a one-pot process in an aqueous medium by heating to 100°C under a nitrogen atmosphere.

2.2.1 Preparation of selenium precursor (NaHSe solution)

The preparation approach used in this experiment is similar to the approach used in the study by İbiş et al.(2026). Firstly, selenium powder (10 mg, 0.13 mmol) was transferred into a two-necked flask under a nitrogen atmosphere at room temperature. In a separate beaker, 22 mg of sodium borohydride (NaBH_4 , 0.45 mmol) was dissolved in 5 mL of DW and purged with nitrogen for 5 minutes to provide an inert environment. This solution was then added to the selenium in the two-necked flask at room temperature, and heated to 80°C . The process included preparing up the freshly prepared solution into a 5 ml syringe and adding it to the core solution, which will be discussed in the following section.

2.2.2 Synthesis of CuInSe₂/ZnS QDs

A detailed illustration of the synthesis is shown in Figure 2.1. For the synthesis of CuInSe₂/ZnS core/shell QDs, first, the core reaction mixture was prepared. These solutions were prepared separately: 42.2 mg (0.145 mmol) of indium (III) acetate was dissolved in 0.8 mL of ethanol, while 4.9 mg (0.017 mmol) of copper nitrate was dissolved in 0.4 mL of DW. Additionally, a trisodium citrate solution was obtained by dissolving 164 mg of citric acid monohydrate and 400 mg of sodium hydroxide in 0.8 mL of DW. These three separately prepared solutions were combined in a 100 mL three-necked flask. Subsequently, 16 mg (0.098 mmol) of NAC was added as a capping agent, followed by the addition of 40 mL of DW. The pH of the core solution is adjusted to 8 using 0.001 M NaOH, and the solution is placed in an oil bath under a nitrogen atmosphere. Following this step, 5 mL of the NaHSe solution, the preparation of which was described in the previous section, was added to the core solution in the oil bath using a syringe, and the mixture was heated to 100°C and stirred for 45 minutes. The shell precursor solution was prepared by dissolving 379.2 mg (2.330 mmol) of NAC, 120.7 mg (1.580 mmol) of thiourea, and 340.2 mg (1.139 mmol) of zinc nitrate hexahydrate in 10 mL of DW. After preparation steps the pH value of the shell solution is 2.5. After the 45 minute core growth, this shell solution was added. Stirring was continued for an additional 45 minutes under the same conditions. After a total reaction time of 1.5 hours, the final product was collected by centrifugation at 14,000 rpm for 3 minutes and stored in solid form at 2-8°C. In the study (İbiş et al. 2026), nearly identical method was applied with minor modifications. The effects of different capping agents were investigated by substituting NAC with 3-MPA and L-GSH under the same conditions. Their chemical structures are shown in Figure 2.2. Additionally, the roles of precursor stoichiometry were also studied by independently doubling the copper and indium precursor amounts for each capping agent.

The synthesized QDs were photographed in both colloidal and solid forms under 365 nm UV illumination and sunlight, as shown in Figure 2.3. In main reactions, the one with the NAC ligand exhibits a red emission under UV light, while L-GSH and 3-MPA appear orange in color. When the amount of copper is doubled, no luminescence is observed for the NAC and L-GSH capped QDs, whereas the 3-MPA-capped QD showed an orange luminescence. Similarly, when the amount of indium is doubled, an

orange luminescence is observed for the L-GSH and 3-MPA, while no luminescence is present for the NAC capped QDs.

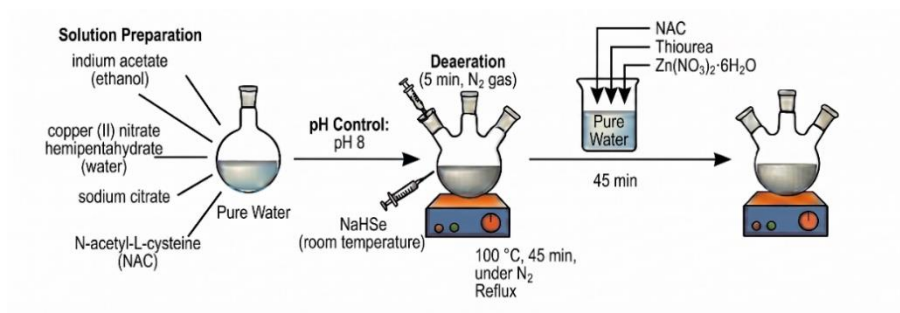


Figure 2.1 : The detailed synthesis route.

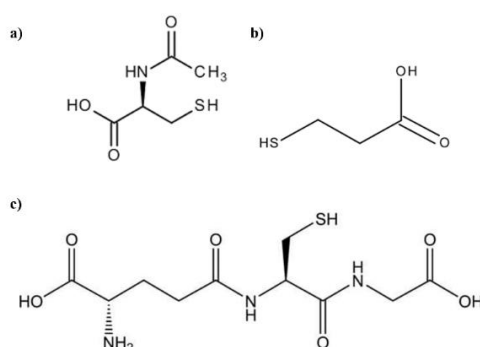


Figure 2.2 : Chemical structure of a) NAC b) 3-MPA c) L-GSH.

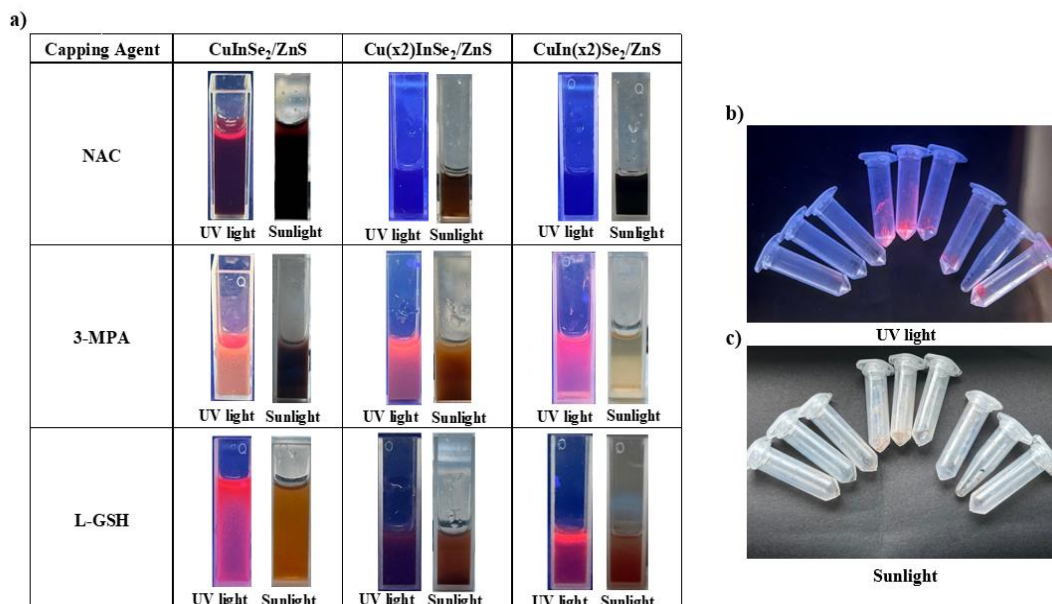


Figure 2.3 : a) The color of each QD under sunlight and UV-light b) UV light and c) sunlight photographs of the solid state QDs capped with NAC (left), 3-MPA (middle), and L-GSH (right). Within each capping group, tubes are ordered from left to right as stoichiometric main reaction, Cu-rich, and In-rich formulations.

2.3 Effect of pH On The Optical Properties And Stability of QDs

A series of DW solutions with pH values ranging from 5 to 11 were prepared using 0.001 M NaOH, 0.001 M HCl. The QDs were then dispersed in these solutions at a ratio of 1 mg of QD per 1 mL of pH solution, and their optical properties were characterized via photoluminescence spectroscopy (PL) and UV-Vis spectroscopy.

2.4 Adsorption Experiments

Three different organic dyes were selected based on their ionic characteristics. Methylene Blue (MB) was employed as a cationic model and Methyl Orange (MO) as an anionic model, whereas Rhodamine B (RB) was a zwitterionic model exhibiting cationic character depending on the pH conditions. The main purpose of this experiment is to examine the interaction between dyes and CuInSe₂/ZnS QDs.

2.4.1 Dye solution preparation

Stock solutions for each dye were prepared at a concentration of 25 μ M in 50 mL of deionized water. To prevent photodegradation, these solutions were stored in the dark at 2-8°C.

2.4.2 Experimental procedure of interaction between QDs and dyes

The adsorption experiments were conducted using a standardized ratio of 1 mg of QDs per 1 mL of dye solution. The QD-dye mixtures were shaken at 200 rpm for 2 hours with a laboratory shaker. Before optical characterization, a 500 μ L sample was collected from the mixture and centrifuged at 14,000 rpm for 1 minute. After centrifugation, 0.4 mL of supernatant was taken and diluted with 2.1 mL of DW. The final solutions were analyzed using UV-Vis spectroscopy.

2.5 Desorption Experiments

These procedures were aimed to observe the release of adsorbed dye molecules back into the liquid phase using thermal and solvent based desorption methods.

2.5.1 Experimental procedure of thermal based desorption

In this method, DW (1 mL) was added to the QDs (1 mg) after dye adsorption study. Subsequently, the mixture was shaken in a water bath at 50 °C for 30 minutes.

2.5.2 Experimental procedure of solvent based desorption

For solvent based desorption method, methanol was used as a solvent. 1 ml of methanol was added to the QDs (1 mg) adsorbed with dye and stirred in a shaker at 200 rpm for 30 minutes.

2.6 Characterization Methods and Equipment

The characterization methods used in order to evaluate the structural and optical characteristics of synthesized QDs are summarized. RIGAKU SmartLab X-ray diffraction (XRD) spectrometer measurements were carried out to evaluate the structural properties and crystallinity of the QDs.

The surface characteristics of the pure QDs and dye adsorbed QDs structures were analysed using a PerkinElmer ATR-FTIR. The photoluminescence spectra were obtained and the chemical structure and bonds of CuInSe₂/ZnS QDs were investigated from the solid product using a RENISHAW inVia Raman spectrometer with 457 nm excitation laser, 0.01% laser power, 10 s acquisition time, and x50 objective lens at room temperature.

The characterization of the optical properties of QDs and changes in the dye concentration in the liquid phase after adsorption and desorption studies were analysed by Varian Cary Eclipse fluorescence spectrofluorometer and N4S/N4 UV-Visible Spectrophotometer.



3. RESULTS AND DISCUSSION

3.1 The Structural Properties of CuInSe₂/ZnS QDs

XRD, FTIR and Raman analysis were used to investigate the structural properties of QDs. Figure 3.1 shows the XRD spectra used to examine the crystallinity of CuInSe₂/ZnS.

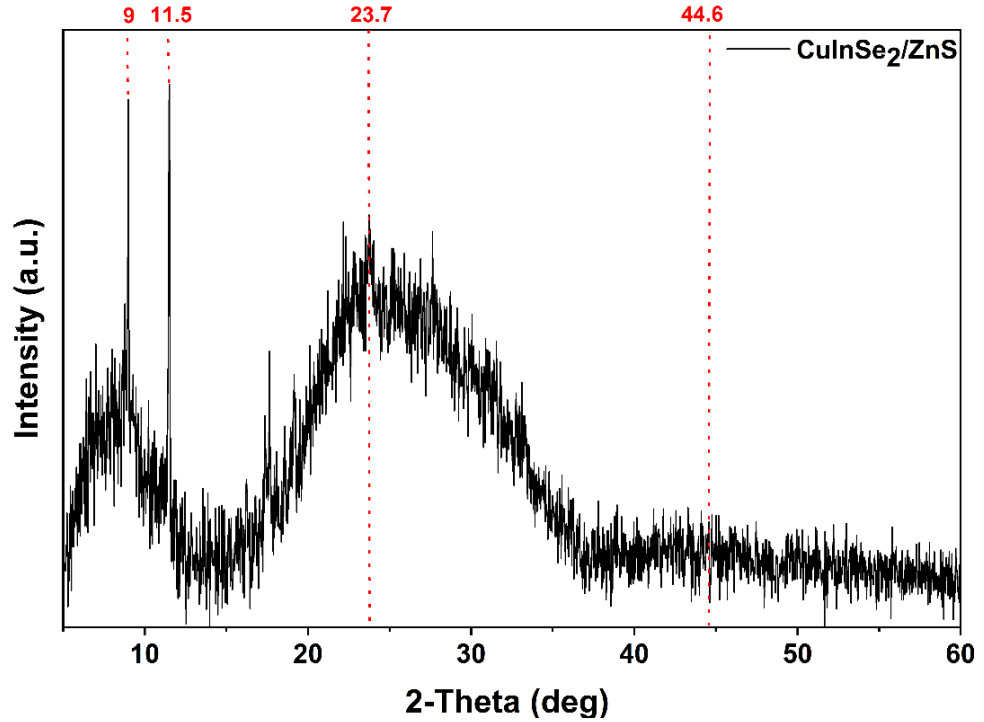


Figure 3.1 : XRD spectra of CuInSe₂/ZnS.

Standard chalcopyrite CuInSe₂ nanocrystals typically exhibit primary diffraction peaks at approximately 27°, 45°, and 51°, corresponding to the (112), (220), and (312) planes, respectively (JCPDS No. 40–1487) (Ghali et al., 2016). ZnS shell's characteristic peaks at 28°, 48°, and 56°, corresponding to the (111), (220), (311) planes, respectively (JCPDS: No. 05-0566) (Gusain et al., 2021; ICDD PDF No: 89-5649; Zhong et al., 2011). The CuInSe₂/ZnS core/shell QDs shown in Figure 3.1 exhibited a broad diffraction angle centered at 23.7°, together with a weak peak around 44°. The significant peak broadening and reduced diffraction intensity are attributed

to the nanoscale dimensions of the particles and the ZnS shell coating, which partially masks the diffraction features of the CuInSe₂ core, by the fact that in core/shell structures, the shell effect can cause broadening of the peaks and a decrease in intensity (Huang et al., 2021). These findings indicate that the material is a quantum dot and the synthesis was carried out successfully. Additional diffraction angles at $\sim 9^\circ$ and $\sim 11^\circ$ do not correspond to the characteristic diffraction angles of chalcopyrite CuInSe₂ core crystal structure and they are attributed to surface-bound organic ligands organic molecules that are unrelated to the crystal structure of the material and might arise from the assemblies that exist there (Liu et al., 2019).

The surface chemistry and functional groups of the QDs were characterized via FTIR analysis. Figures 3.2, 3.3, and 3.4 show the FTIR spectra of NAC, 3-MPA, and L-GSH capped QDs, respectively.

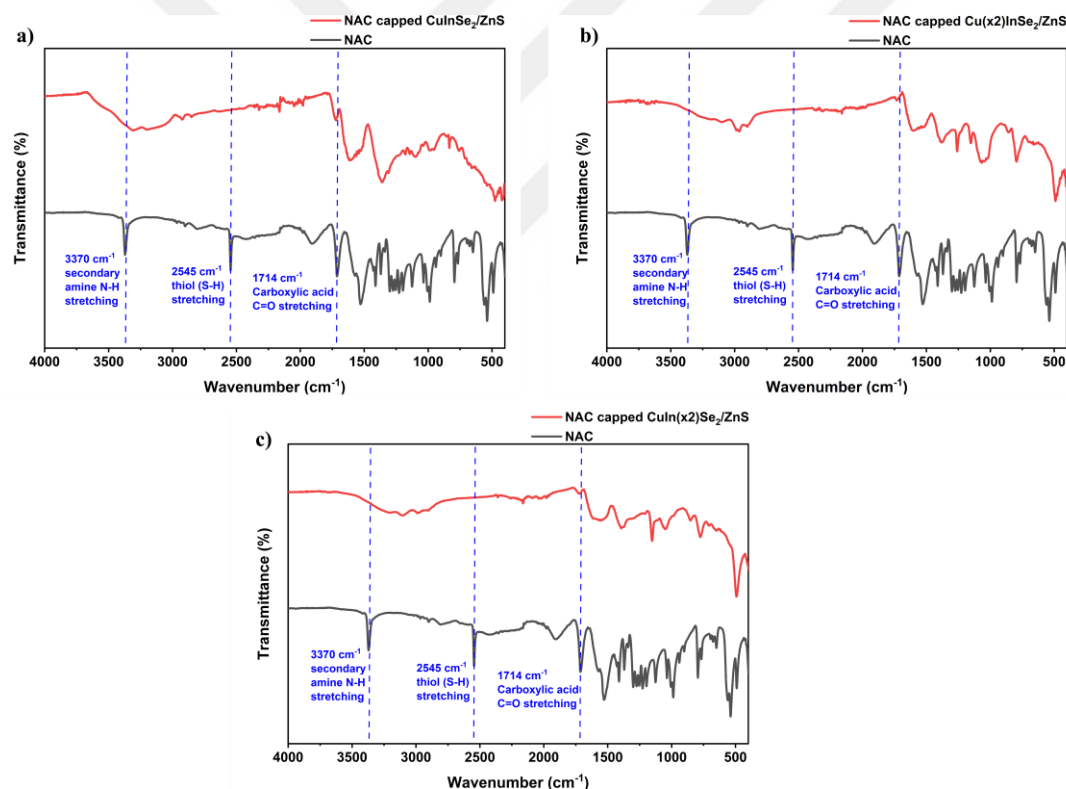


Figure 3.2 : FTIR spectrum of a) NAC capped CuInSe₂/ZnS b) Cu(x₂)InSe₂/ZnS c) CuIn(x₂)Se₂/ZnS.

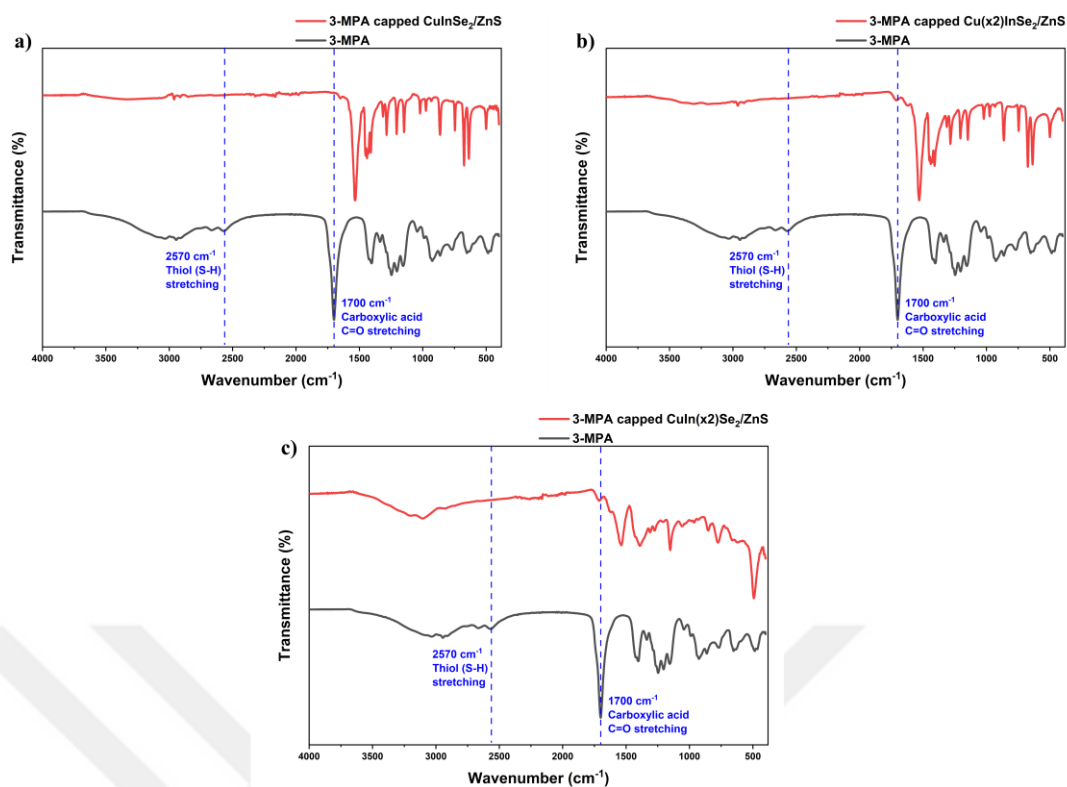


Figure 3.3 : FTIR spectrum of a) 3-MPA capped $\text{CuInSe}_2/\text{ZnS}$ b) $\text{Cu}(x_2)\text{InSe}_2/\text{ZnS}$ c) $\text{CuIn}(x_2)\text{Se}_2/\text{ZnS}$.

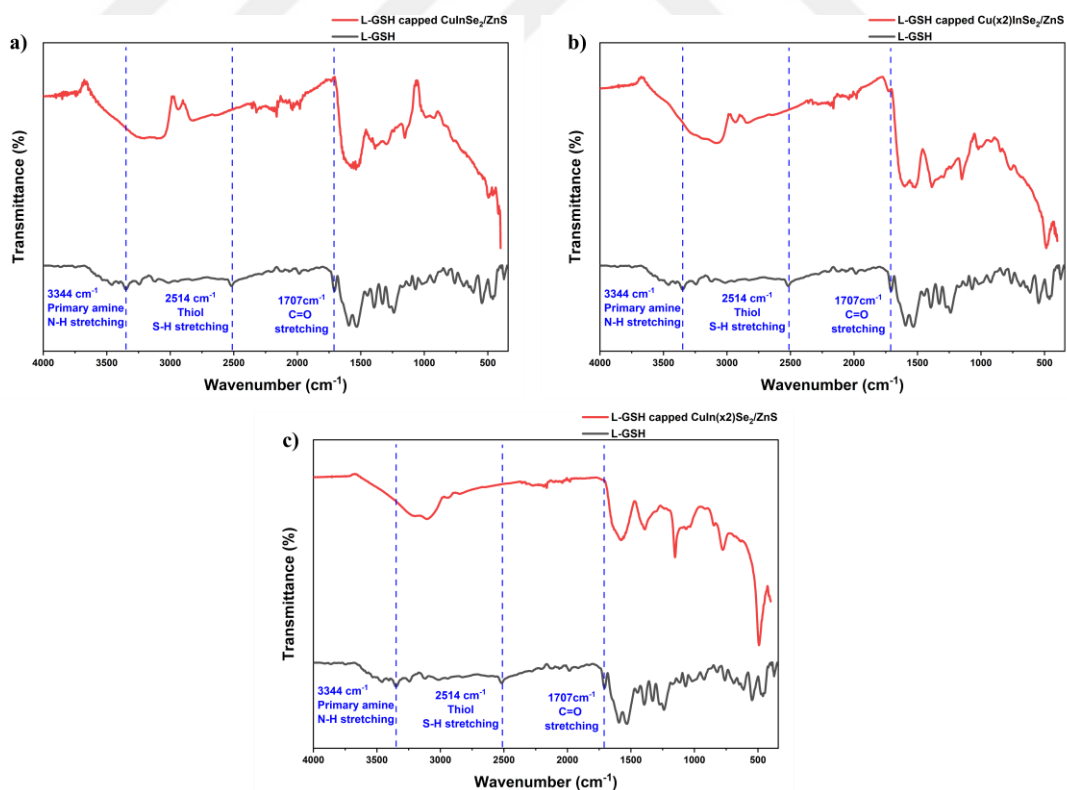


Figure 3.4 : FTIR spectrum of a) L-GSH capped $\text{CuInSe}_2/\text{ZnS}$ b) $\text{Cu}(x_2)\text{InSe}_2/\text{ZnS}$ c) $\text{CuIn}(x_2)\text{Se}_2/\text{ZnS}$.

For Figure 3.2, FTIR analysis indicates that the disappearance of the thiol (S-H) stretching band at 2545 cm^{-1} provides strong evidence for the coordinate covalent bonding of ligands to the QD surface via the sulphur atom. The characteristic secondary amine N-H stretching band at 3370 cm^{-1} and the carboxylic acid C=O stretching band at 1714 cm^{-1} shifts as well as decreases in intensity. A similar result was observed in QDs synthesised with double the amounts of copper and indium; in both cases, the complete lack of the characteristic thiol (S-H) band at 2545 cm^{-1} confirms that coordination occurs through sulphur atom. These findings demonstrate that successful surface passivation was achieved in all three synthesis routes, independent of the precursor stoichiometry.

For Figure 3.3, in all three cases, the disappearance of the characteristic thiol (S-H) stretching vibration at $\sim 2570\text{ cm}^{-1}$ confirms that 3-MPA binds consistently to the QD surface via its thiol group and forms stable sulphur metal bonds, independent of the core precursor stoichiometry. Furthermore, the C=O stretching band from carboxylic acid around 1700 cm^{-1} exhibits a noticeable shift and decrease in intensity after QD formation, indicating the involvement of the carboxyl group in surface interactions.

For Figure 3.4, the L-GSH ligand was coordinate covalently bound to the QD surface via sulphur atom. Peak broadening and shift or absence were observed at 3344 cm^{-1} (N-H stretching) and 1707 cm^{-1} (C=O stretching).

In summary for all spectra, it is obvious that FTIR analysis confirmed the ligands were successfully bound to the surface of all QDs with sulphur, especially as evidenced by the disappearance of the characteristic thiol (S-H) peaks.

Raman and Raman emission spectra are shown in Figure 3.5, 3.6, and 3.7.

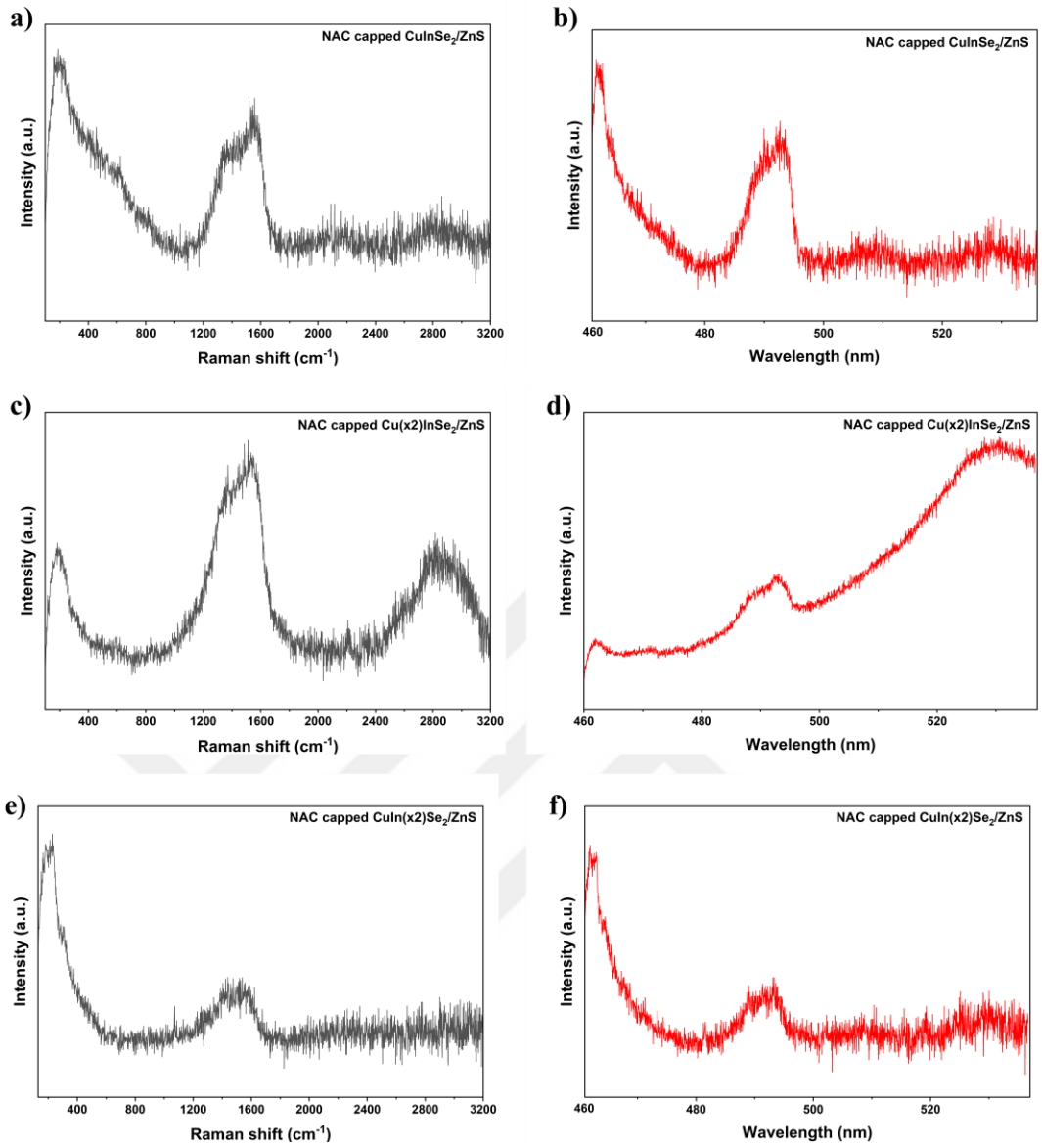


Figure 3.5 : Raman and Raman emission spectra of NAC capped a-b) $\text{CuInSe}_2/\text{ZnS}$, c-d) $\text{Cu}(x_2)\text{InSe}_2/\text{ZnS}$, and e-f) $\text{CuIn}(x_2)\text{Se}_2/\text{ZnS}$.

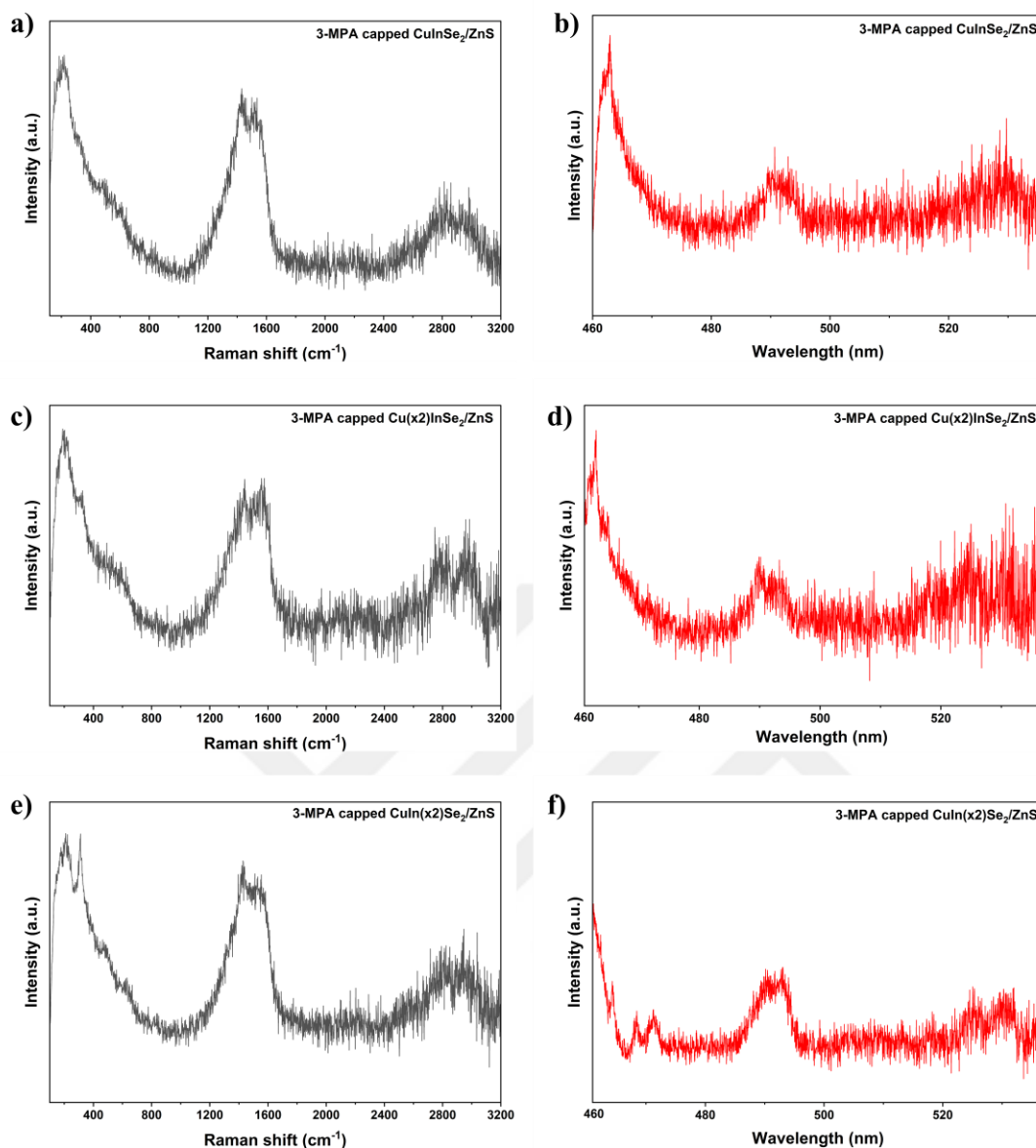


Figure 3.6 : Raman and Raman emission spectra of 3-MPA capped a-b) $\text{CuInSe}_2/\text{ZnS}$, c-d) $\text{Cu}(\text{x}2)\text{InSe}_2/\text{ZnS}$, and e-f) $\text{CuIn}(\text{x}2)\text{Se}_2/\text{ZnS}$.

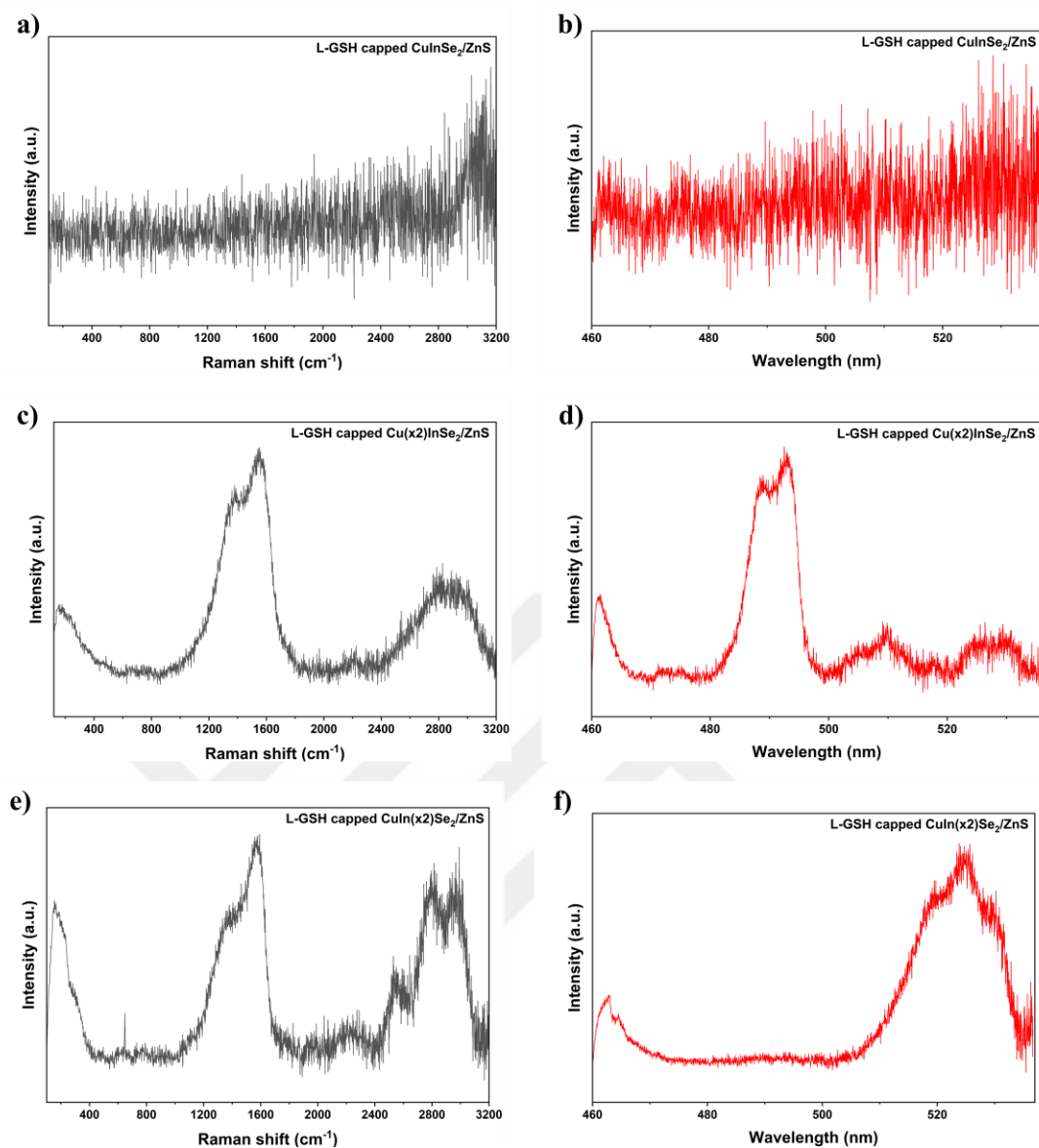


Figure 3.7 : Raman and Raman emission spectra of L-GSH capped a-b) $\text{CuInSe}_2/\text{ZnS}$, c-d) $\text{Cu}(x_2)\text{InSe}_2/\text{ZnS}$, and e-f) $\text{CuIn}(x_2)\text{Se}_2/\text{ZnS}$.

Raman and Raman emission spectra were examined to clarify the structural stability and photoluminescent behaviour of $\text{CuInSe}_2/\text{ZnS}$ QDs. Based on the spectra for all QDs, it is observed that QDs preserve their stability and maintain their characteristic photoluminescence emission properties under laser excitation. This is a significant observation because if the QDs had degraded or not kept their stability, photoluminescence emission would not be expected.

3.2 The Optical Properties of CuInSe₂/ZnS QDs

In Figure 3.8 , absorption and emission spectra are illustrated for the characterization of the optical properties of CuInSe₂/ZnS QDs, with selected optimum pH values for each within the 200-850 nm wavelength range.

The study was conducted at pH values ranging from 5 to 11; all emission values correspond to excitation at 450 nm, and it was observed that the QDs emitted at approximately 680 nm at pH values where solubility was observed.

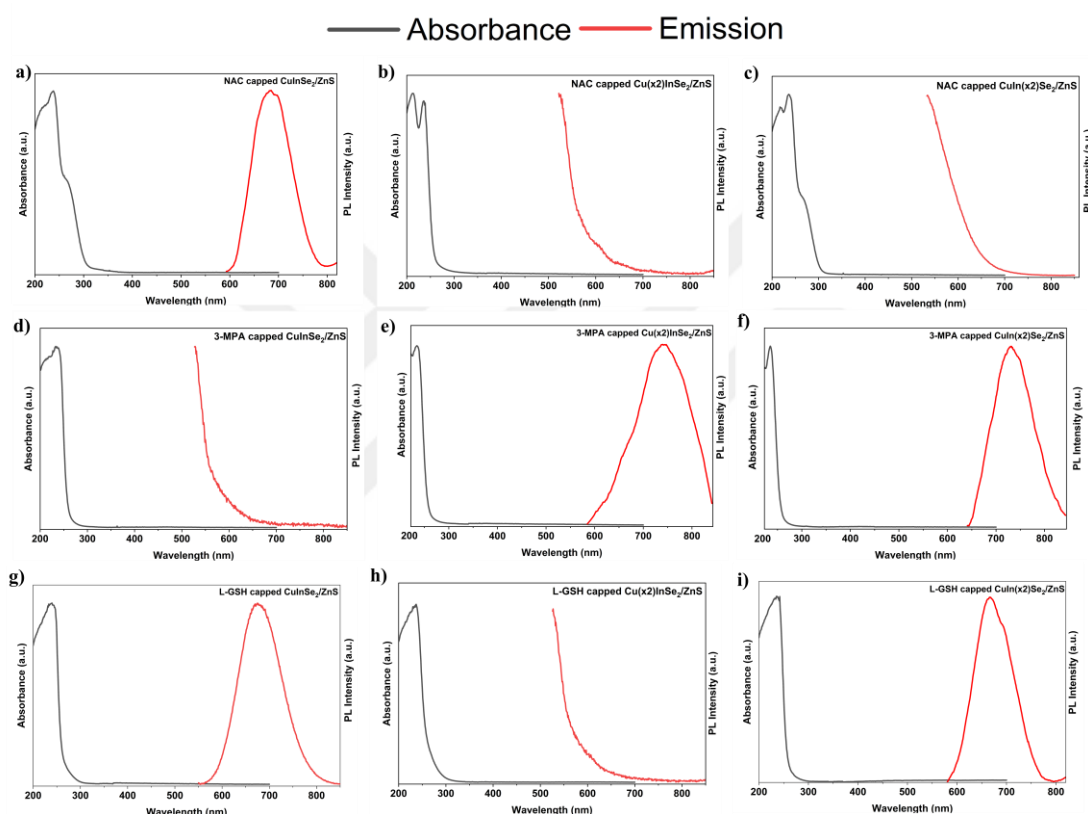


Figure 3.8 : UV-Vis absorption (black lines, left y-axis) and photoluminescence (PL) emission (red lines, right y-axis) spectra of CuInSe₂/ZnS QDs at their optimized pH values: a-c) NAC-capped, d-f) 3-MPA-capped, and g-i) L-GSH-capped. The metal compositions correspond to core ratios of a, d, g) CuInSe₂, b, e, h) Cu(x₂)InSe₂ and c, f, i) CuIn(x₂)Se₂.

In Figure 3.9, the solubility of QDs at seven different pH (5 to 11) values has been also examined using PL spectroscopy.

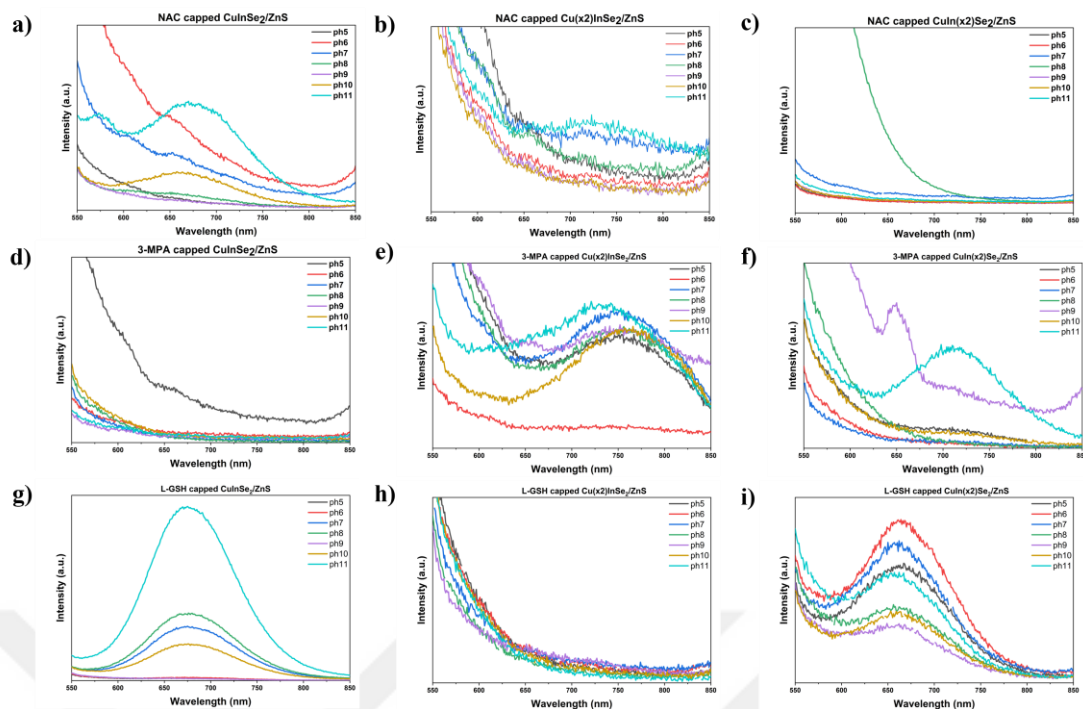


Figure 3.9 : PL spectra of a-c) NAC-capped, d-f) 3-MPA-capped, and g-i) L-GSH-capped QDs (main, Cu-rich, and In-rich from left to right) at pH 5–11 under 450 nm excitation wavelength.

Among all these results, it is particularly clear that L-GSH capped $\text{CuInSe}_2/\text{ZnS}$ remain suspended in a colloidal state in water at pH 11 without agglomeration.

In conclusion, it is important to analyze the pH values at which QDs dissolve or do not dissolve for adsorption studies with organic dyes, and this is why it was investigated.

The solubility behavior of the QDs did not exhibit a consistent trend, limiting their potential application as pH sensors. However, their relatively low solubility proved advantageous for adsorption studies, which constituted the primary focus of this thesis.

3.3 Adsorption Studies

The adsorption efficiencies of QDs for three different types of dye were evaluated using UV-Vis spectrophotometric analysis, and the samples were analysed by FTIR following dye adsorption. Chemical structures of dyes used were MB, RB and MO shown in Figure 3.10. The interaction mechanisms between the QD surfaces and the dye molecules are expected to be strongly influenced by the ionic nature of both the dyes and the QD surfaces.

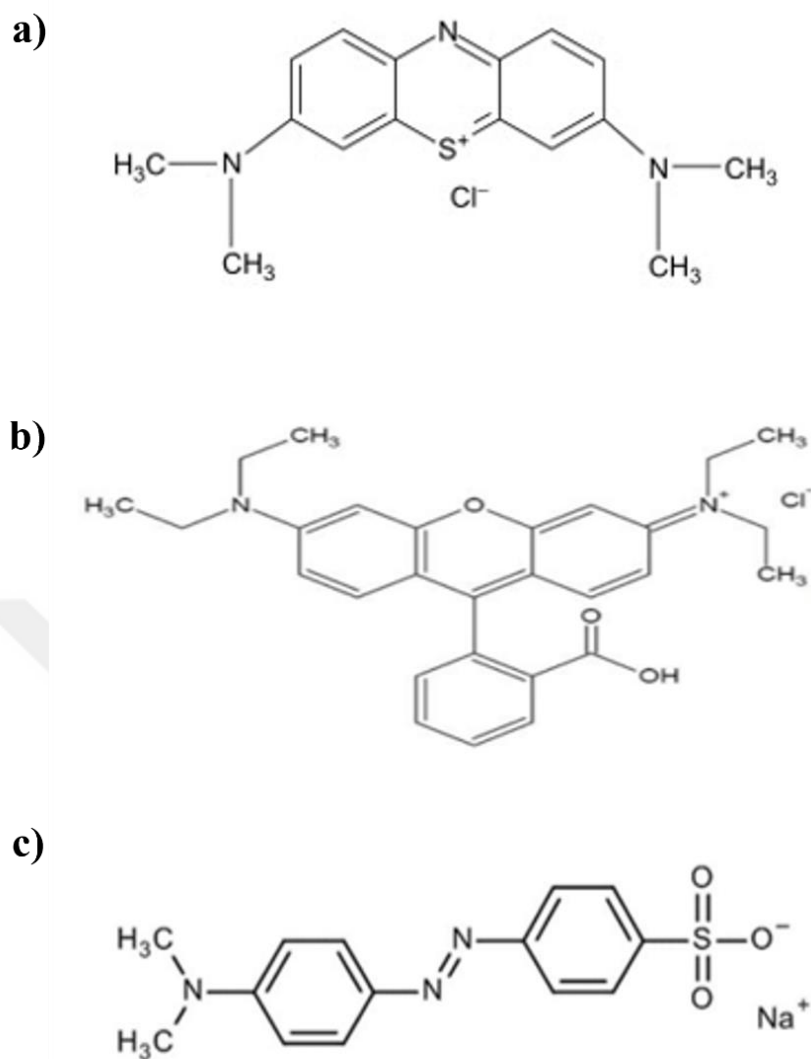


Figure 3.10 : Chemical structure of a) MB b) RB c) MO.

Figures 3.11, 3.12, and 3.13 shows the UV-Vis absorption spectra and the corresponding solution photographs for the adsorption of MB, RB, and MO, respectively.

3.3.1 Methylene blue adsorption studies

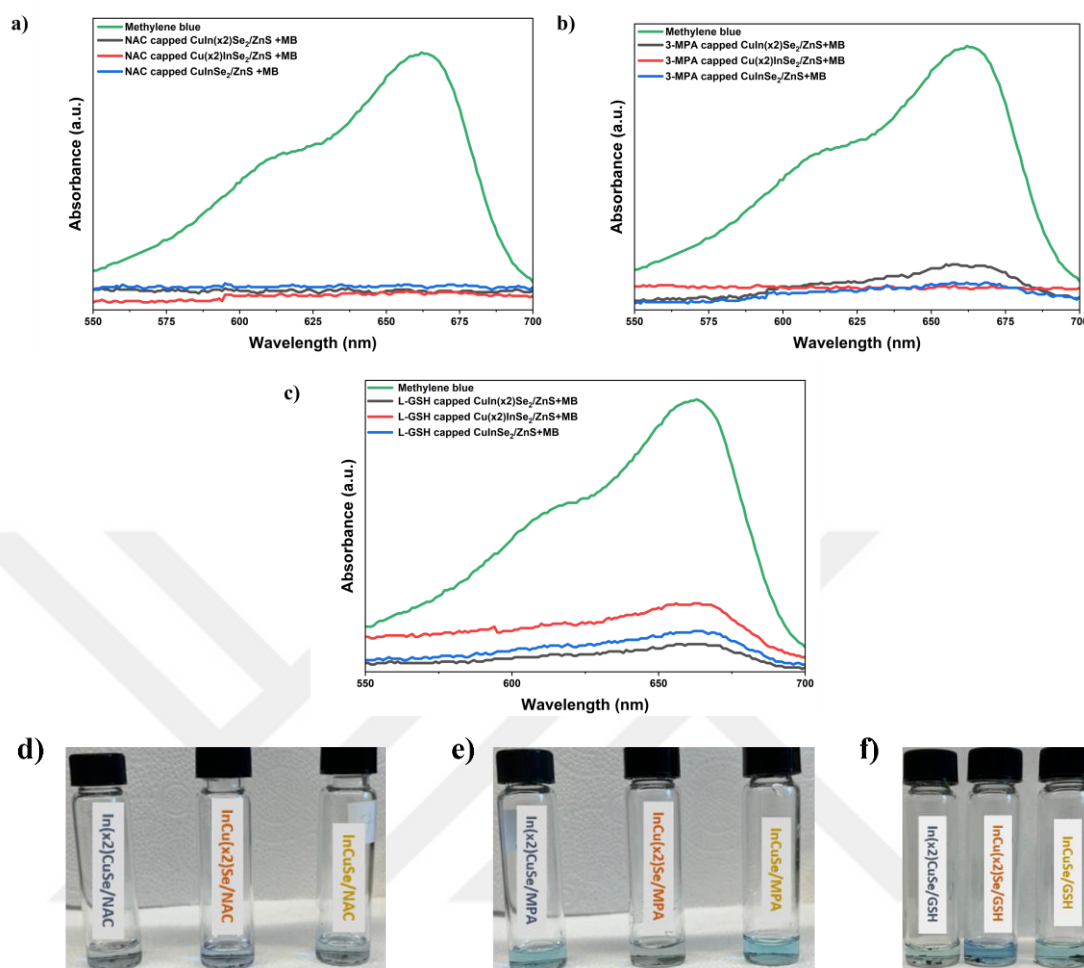


Figure 3.11 : Absorption spectra of MB dye with a) NAC, b) 3-MPA, and c) L-GSH capped QDs. d-f) The images represent dyes + QDs after 2 hours shaking.

The UV spectra are obtained based on the amount of remaining dye in the solution; a decreased peak intensity indicates that the amount of dye remaining in the solution is low, meaning that as the absorbance intensity decreases, dye adsorption abilities of QDs becomes higher. As shown in Figure 3.11, the dye adsorption performance of three different ligands capped QDs is ranked from highest to lowest, the order is NAC, 3-MPA, and L-GSH. Since MB is cationic dye, it is expected to occur an electrostatic interaction between QDs surface and dye molecule. Another fact is that the color changes observed in the corresponding images clearly support this strong interaction. In conclusion, for all QDs, the negative charges from the functional groups on the QDs surface effectively adsorbed the cationic dye molecules via electrostatic attraction particularly and it is also clear that the interaction with MB was very strong for all of them.

3.3.2 Rhodamine B adsorption studies

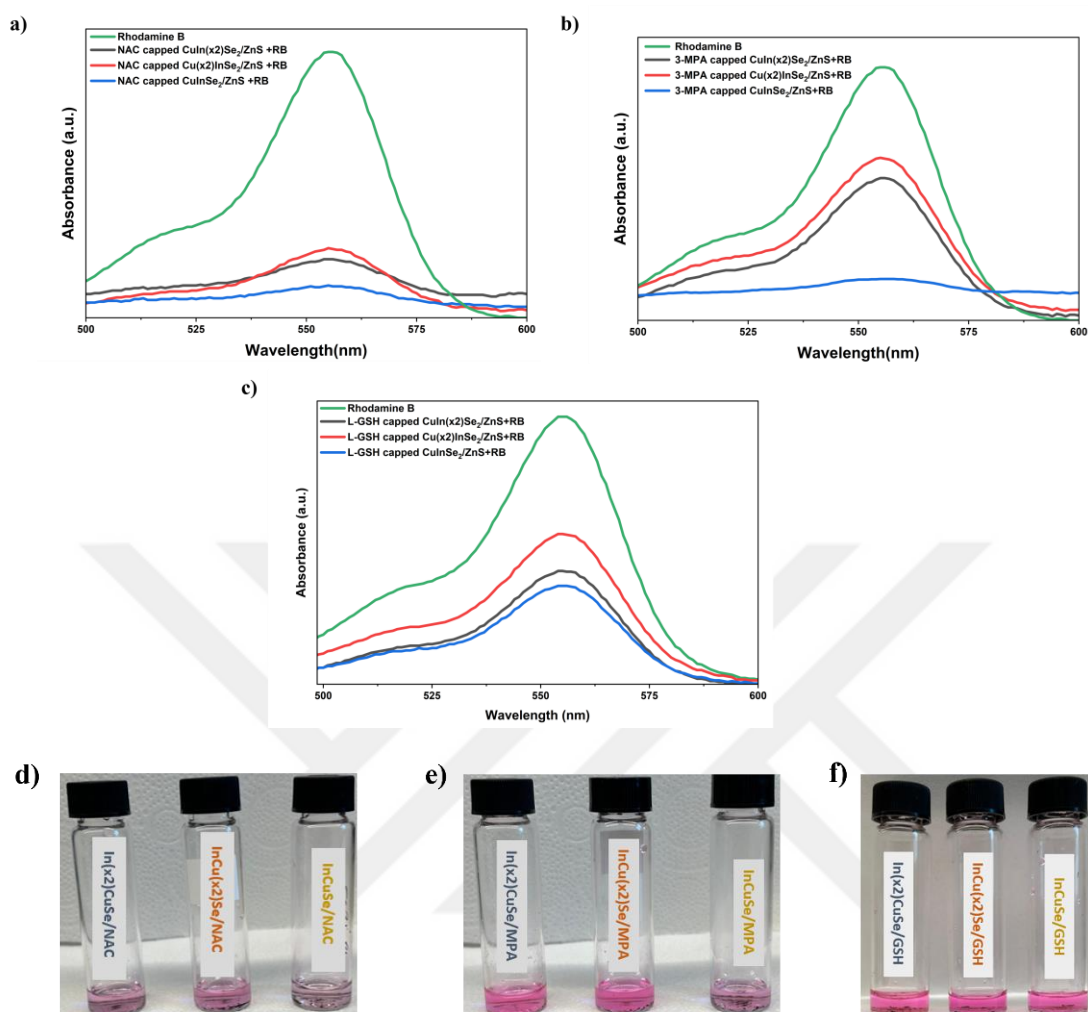


Figure 3.12 : Absorption spectra of RB dye with a) NAC b) 3-MPA, and c) GSH-capped QDs. d-f) The images represent dyes + QDs after 2 hours shaking.

RB is a type of dye that exhibits partially cationic properties depending on the pH value and is referred as a zwitterionic; this dye also exhibits a similar discoloration tendency, although the decrease in absorbance intensity was generally less pronounced than observed for MB. This difference is considered that, although electrostatic attraction remains the primary mechanism for the adsorption of the dye molecule, RB's larger molecular structure and steric hindrance may prevent it from reaching some active regions on the QD surface. When interactions with the three different ligands are ranked against each other, the best adsorption results are observed in QDs capped with the NAC ligand, followed by those coated with 3-MPA and L-GSH, as indicated by both the UV spectra and the color change in the images.

3.3.3 Methyl orange adsorption studies

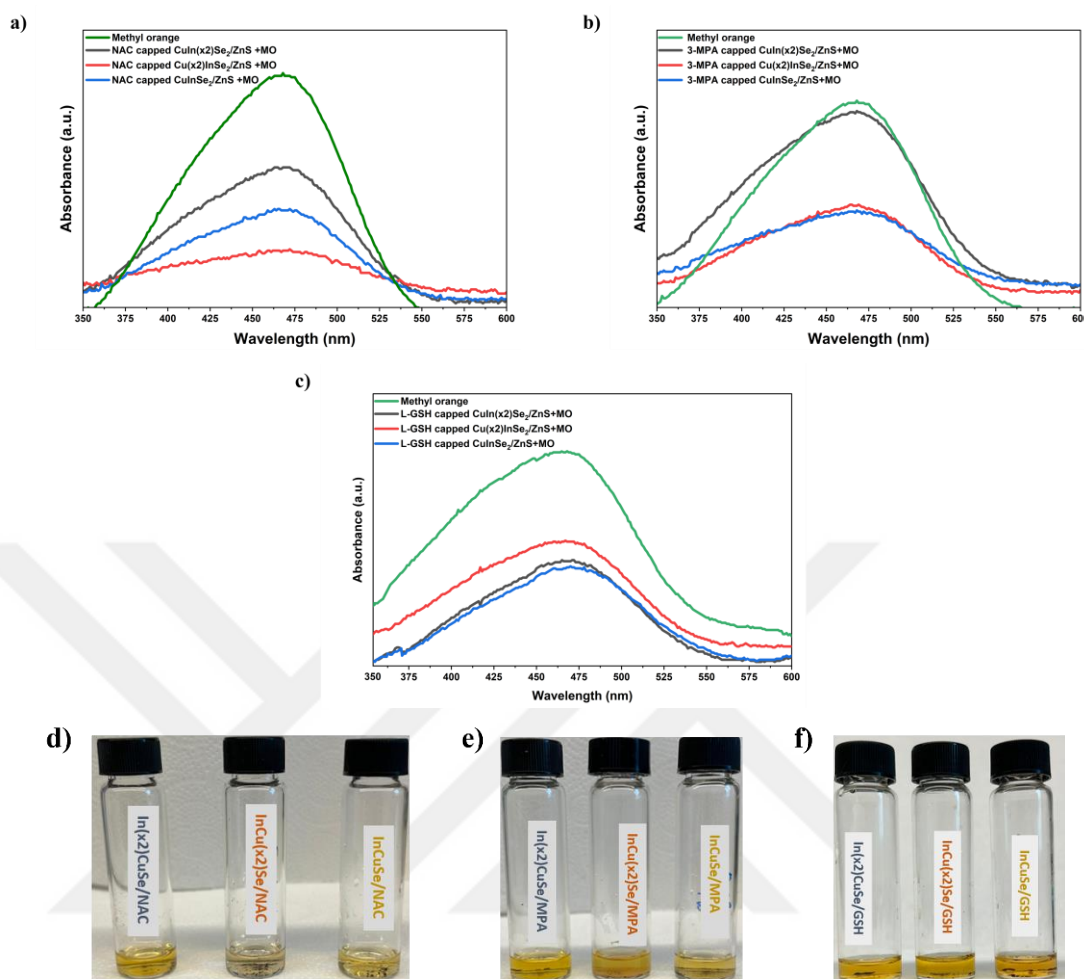


Figure 3.13 : Absorption spectra of MO dye with a) NAC b) 3-MPA, and c) GSH-capped QDs. d-f) The images represent dyes + QDs after 2 hours shaking.

The UV spectra clearly shows that MO exhibits the lowest adsorption efficiency compared to the other two dyes. MO is an anionic dye, and its absorbance peaks have decreased significantly less than those of the cationic dyes; moreover, the visual differences in the solutions are less noticeable. The electrostatic repulsion interactions between the negatively charged sulfate groups on MO molecules and the carboxylate groups on ligand capped QD surfaces can be explained as the primary cause of this performance decline. The lowest binding affinity for MO was observed with QDs capped with 3-MPA; this demonstrates how ligand's specific charge densities can hinder the removal of anionic pollutants.

To quantify dye removal performance, the areas under the UV curves plotted in Origin software were calculated using the equation 3.1.

$$\% \text{ Removal Efficiency} = \frac{A_0 - A_t}{A_0} \times 100 \quad (3.1)$$

In this equation, A_0 represents the absorbance value of the pure dye, corresponding to the area under its peak, while A_t refers to the absorbance peak after adsorption. The dye removal efficiency data for QDs against three structurally diverse organic dyes were summarized in Table 3.1.

Table 3.1 : The removal efficiencies of QDs for MB, RB, and MO.

	MB (%)	RB(%)	MO (%)
NAC capped CuInSe ₂ /ZnS	91.9	88.1	55.6
NAC capped CuIn(x2)Se ₂ /ZnS	95.3	73.3	36.9
NAC capped Cu(x2)InSe ₂ /ZnS	99.1	76.6	71.6
3-MPA capped CuInSe ₂ /ZnS	96.1	79.5	55.4
3-MPA capped CuIn(x2)Se ₂ /ZnS	90.1	44.8	3.4
3-MPA capped Cu(x2)InSe ₂ /ZnS	93.6	33.2	53.2
L-GSH capped CuInSe ₂ /ZnS	84	63.9	70
L-GSH capped CuIn(x2)Se ₂ /ZnS	89.4	59.6	65
L-GSH capped Cu(x2)InSe ₂ /ZnS	68.9	42.4	48.9

The results obtained indicate that the adsorption mechanism varies depending on the dye charge, molecular structure, and ligand type. Among the three dye types, the highest interaction was found in NAC capped Cu(x2)InSe₂/ZnS QDs with MB dye, with a removal efficiency of 99.1%, while the lowest interaction was observed for MO adsorption by 3-MPA capped CuIn(x2)Se₂/ZnS, with a removal efficiency of 3.4%. For RB, in addition to electrostatic interactions, aromatic interactions and surface compatibility are also important parameters affecting the adsorption mechanisms. Furthermore, the structural geometry of the nine different QDs also plays a critical role; for example, the bulky tripeptide structure of L-GSH provides a steric hindrance that partially prevents dye molecules from accessing the QD surface.

3.3.4 FTIR analysis results after adsorption

The adsorption mechanism and the interactions occurring were analyzed using FTIR to identify the functional groups in the structure. The FTIR spectra of the QDs in their pure form and after adsorption with MB, RB, and MO dyes are shown in Figures 3.14, 3.15, and 3.16, respectively.

3.3.4.1 FTIR analysis methylene blue adsorbed QDs

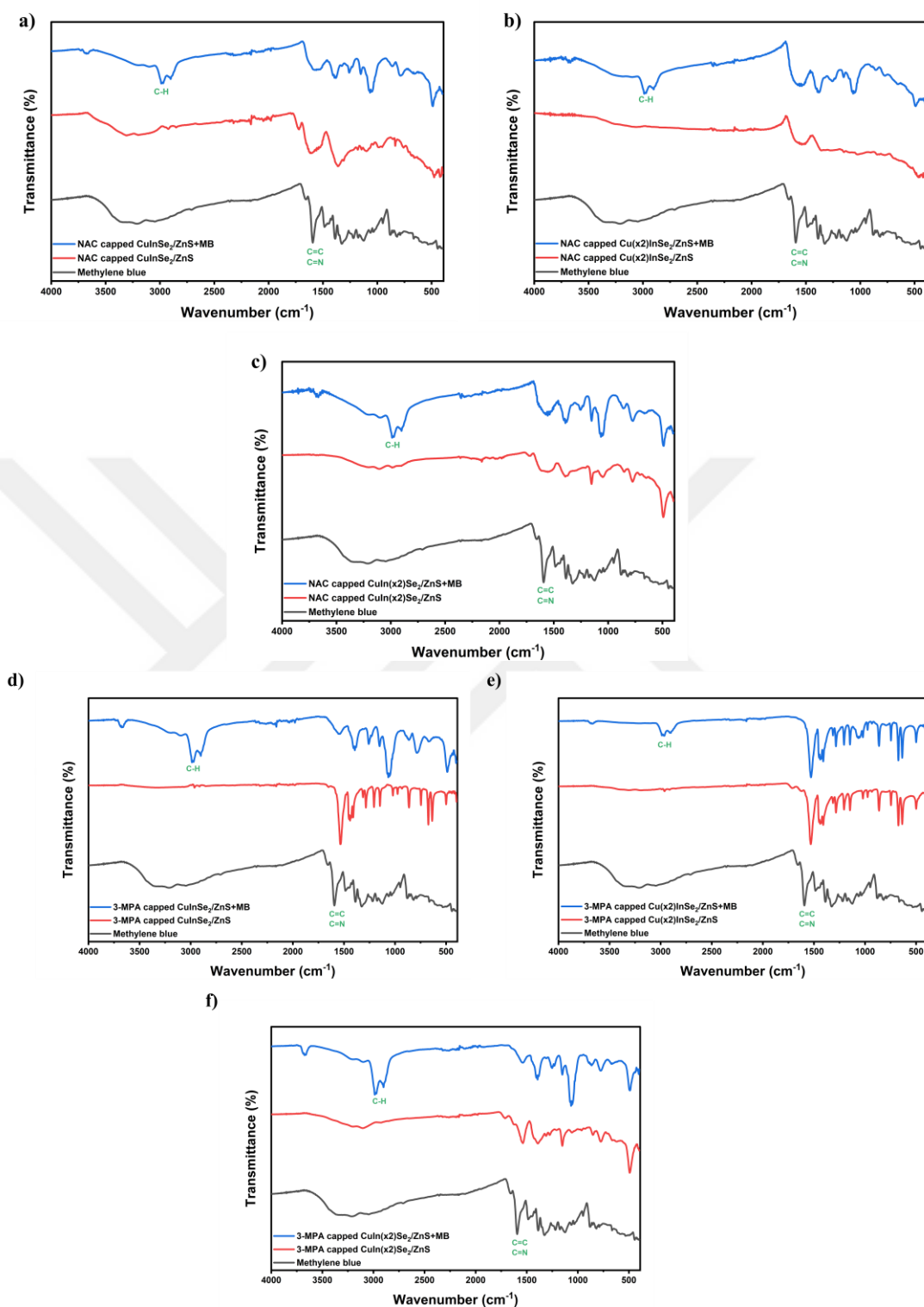


Figure 3.14 : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after MB adsorption.

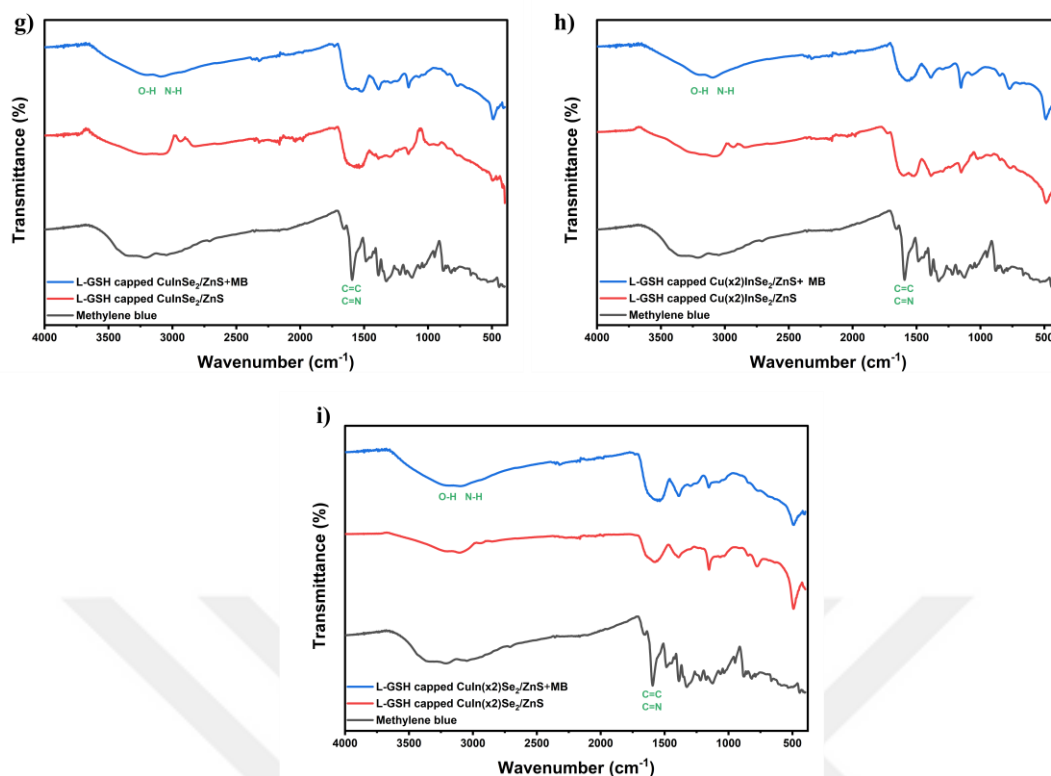


Figure 3.14 (continued) : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after MB adsorption.

For NAC capped QDs, the peaks associated with the aromatic ring in the dye at 1600 cm^{-1} become broader after the interaction. The peaks in the $2900\text{--}3000\text{ cm}^{-1}$ region, which were previously more diffuse C-H peaks, showed a sharp peak following interaction with the positively charged dye, providing strong evidence of electrostatic interaction. This process mainly governed by electrostatic interactions between the cationic dye and negatively charged carboxylate groups on the QD surface, supported by hydrogen bonding and possible $\pi\text{--}\pi$ interactions. For 3-MPA capped QDs, the fingerprint region exhibits sharper peaks because the ligand structure does not contain an amide group like NAC does. The shift of the peaks around 1600 cm^{-1} observed in the spectrum after adsorption indicates an electrostatic interaction between the carboxylate and N^+ in the MB structure. The band observed at $1050\text{--}1090\text{ cm}^{-1}$ can be attributed mainly to C-N stretching vibrations of MB, with possible contributions from C-O vibrations of surface carboxylate ligands. The changes in intensity and position of this band after adsorption indicate strong interactions between the dye molecules and the QD surface. L-GSH is a larger ligand, it has many functional groups and can bind in multiple places. The peak broadening around 1600 cm^{-1} indicates bonding via

π - π , C=C, and C=N interactions. The broadening of the peaks at 3200 and 3500 cm^{-1} indicates the formation of hydrogen bonds.

3.3.4.2 FTIR analysis rhodamine b adsorbed QDs

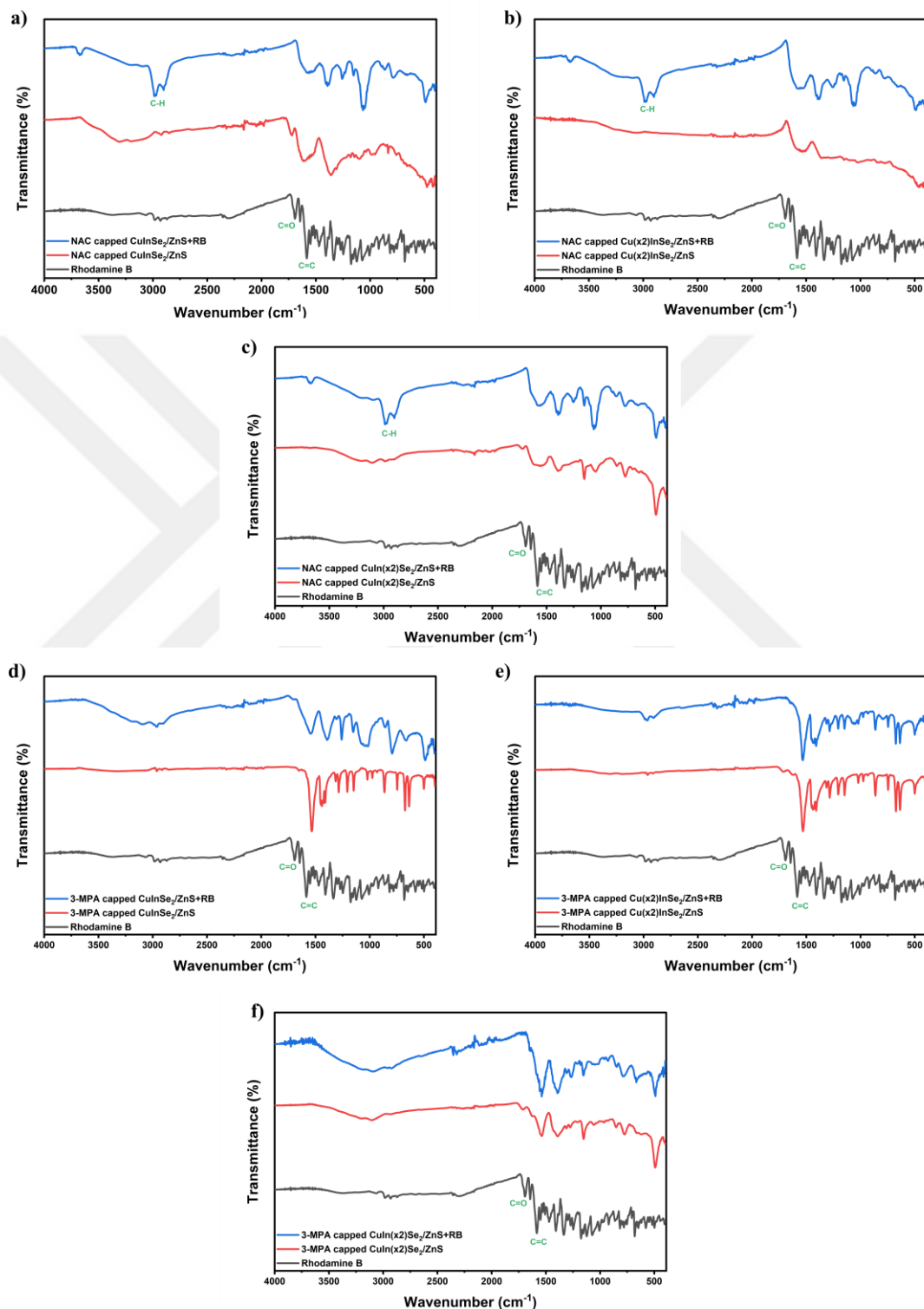


Figure 3.15 : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after RB adsorption.

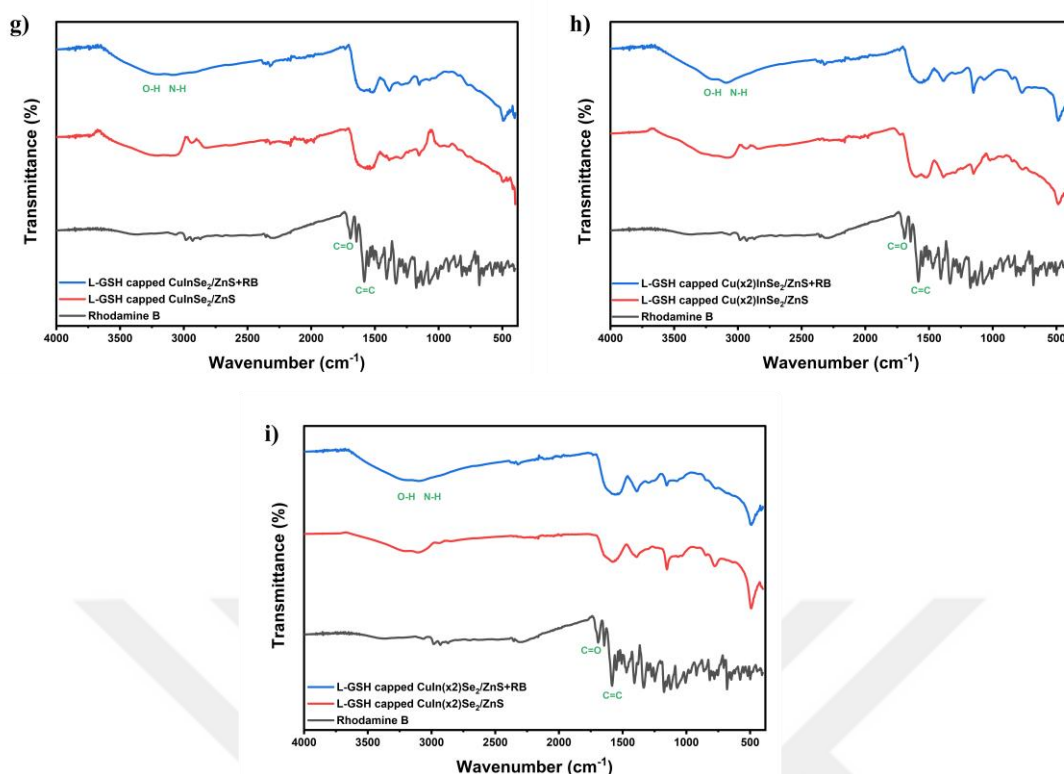


Figure 3.15 (continued) : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after RB adsorption.

RB adsorption on NAC capped QDs exhibits a similar trend, characterized by the shift and broadening of peaks caused by aromatic rings in the dye's molecular structure, indicating that the dye is bound to the QD's surface. Additionally, an electrostatic interaction has occurred between the diethylamino groups in the RB and the carboxylate groups in the ligand, resulting in a broader and shifted peak intensity in the 1500-1600 cm^{-1} range. For 3-MPA capped QDs, the peaks at 1400-1600 cm^{-1} from the aromatic ring of the dye are also observed to shift. When examined in relation to the change in precursor stoichiometry, the decrease in the intensity of the C=O peak of the dye can be explained by the interaction, which involves π - π interaction and the formation of hydrogen bonds, as obtained bond broadening around 3500 cm^{-1} .

For all QDs with the L-GSH ligand, the broad peak observed between 3000 and 3200 cm^{-1} indicates hydrogen bonding between the dye and the QD. The peak at 1600 cm^{-1} which belongs to aromatic ring of the dye became attenuated when adsorbed by L-GSH capped QDs which can be explained by π - π interactions.

3.3.4.3 FTIR analysis methyl orange adsorbed QDs

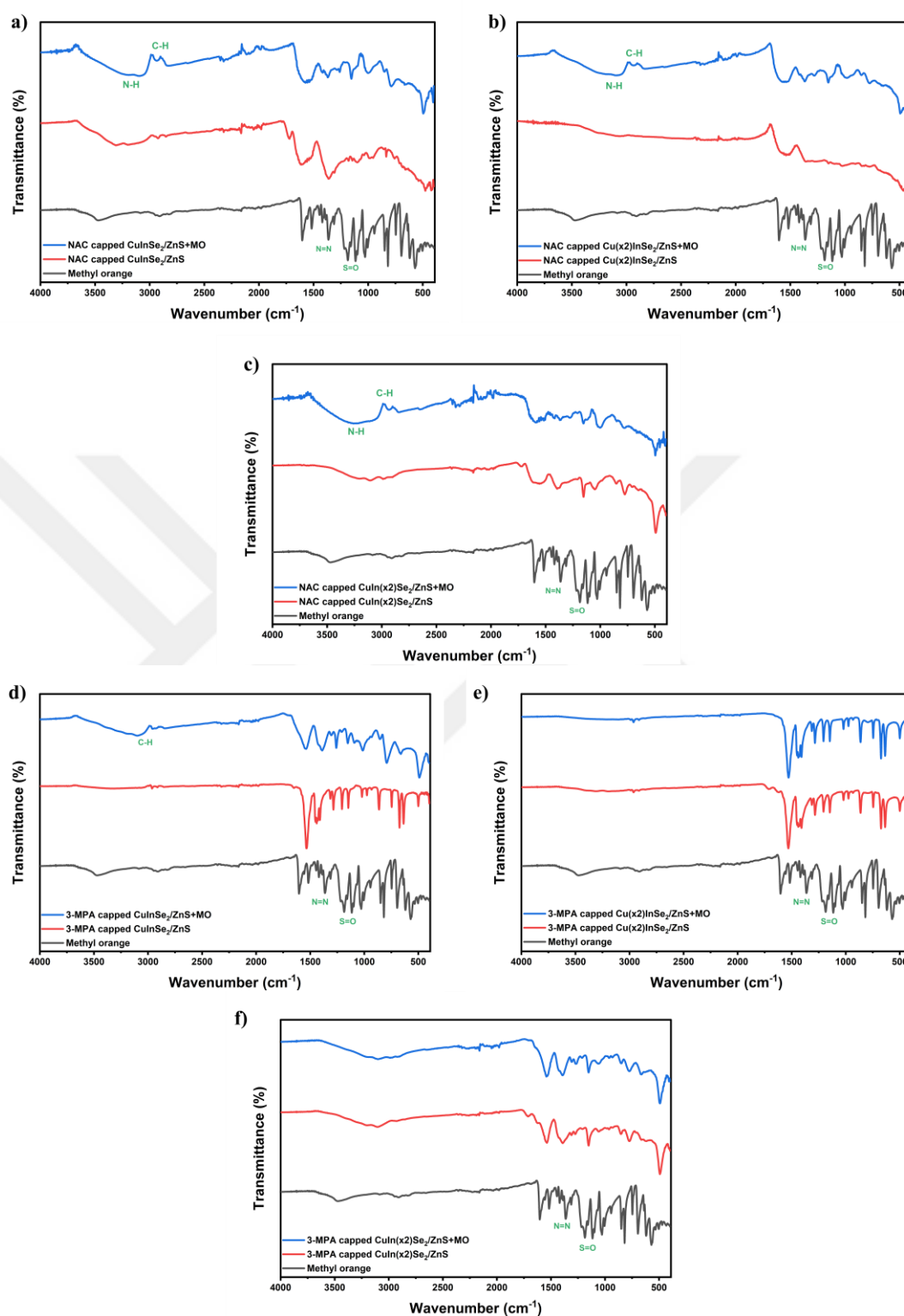


Figure 3.16 : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after MO adsorption.

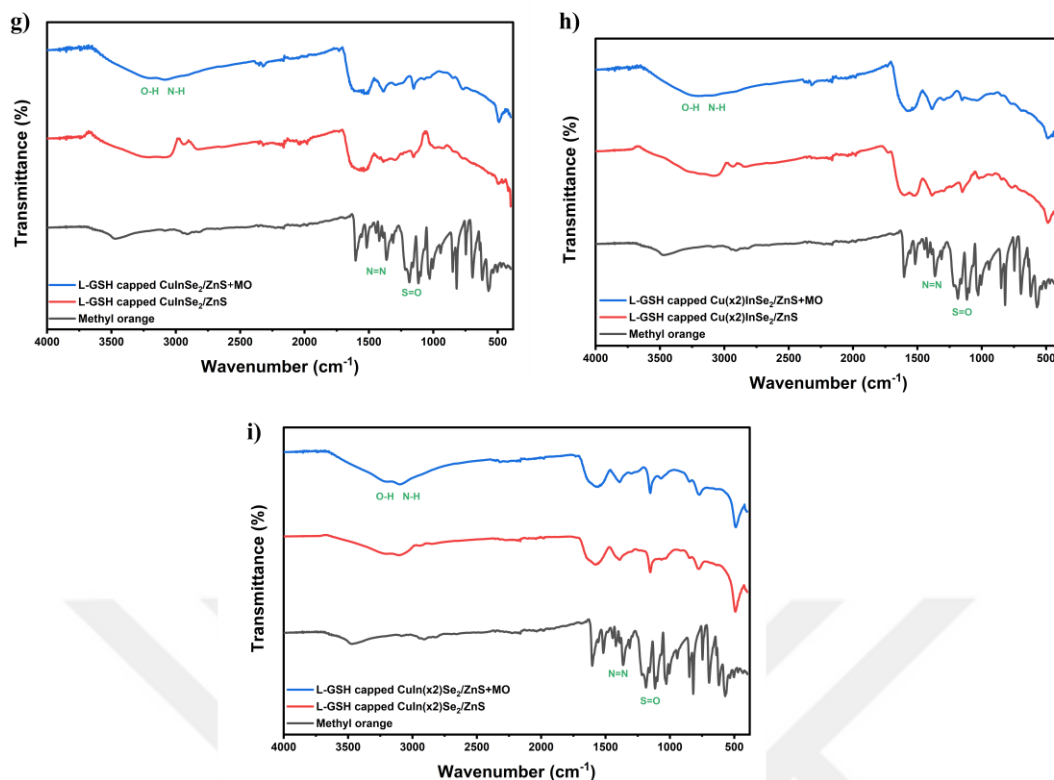


Figure 3.16 (continued) : FTIR spectra of a-c) NAC d-f) 3-MPA g-i) L-GSH capped QDs after MO adsorption.

Since MO is an anionic dye, electrostatic repulsive forces occur between the negatively charged carboxylic acid of the NAC ligand on the QDs and the dye molecule. For this reason, adsorption of MO on the QD surface was expected to be lower than the other dye molecules, which is represented in Table 3.1. Therefore, the interaction between the QD and the dye molecule here is explained by hydrogen bonding. This interaction is considered to involve the azo group of MO, as evidenced by the decrease in peak intensity around 1400 cm^{-1} in the FTIR spectra of QDs+MO. Additionally, hydrophobic interactions between the NAC ligand and the dye molecules may arise due to the presence of hydrophobic moieties, such as the methyl group of NAC and the aromatic benzene rings of the dye molecules. The peak rising around 2900 cm^{-1} for all three stoichiometric ratios of QDs indicates this possible interaction.

Due to the slightly acidic nature of distilled water, which typically has a pH of approximately 5.5–6, the surface of QD may undergo slight protonation during adsorption studies. Therefore, positively charged surface sites can form on the surface of QD, enabling electrostatic interactions with the sulfonate groups of the dye molecule and facilitating adsorption. This was observed as a decrease in peak intensity around 1115 cm^{-1} , the adsorption efficiencies are calculated as around 50% for this

study. The interaction between L-GSH capped QD and the dye is explained primarily by the steric hindrance and the functional groups in L-GSH that can form hydrogen bonds, rather than by electrostatic interactions. The peak broadening around 3000-3200 cm^{-1} in the FTIR spectra of QD+MO, which was attributed to hydrogen bonding, supports this explanation.

Overall, the QD-dye interactions observed in this study were involved primarily by electrostatic attraction and π - π interactions, with possible contributions from specific surface interactions, rather than by weak van der Waals forces alone.

3.4 Desorption Studies

The UV-Vis spectra for desorption studies conducted using methanol as a desorption solvent. The spectra for MB interacted with QDs and the pure dye as a reference for comparison are shown in Figure 3.17.

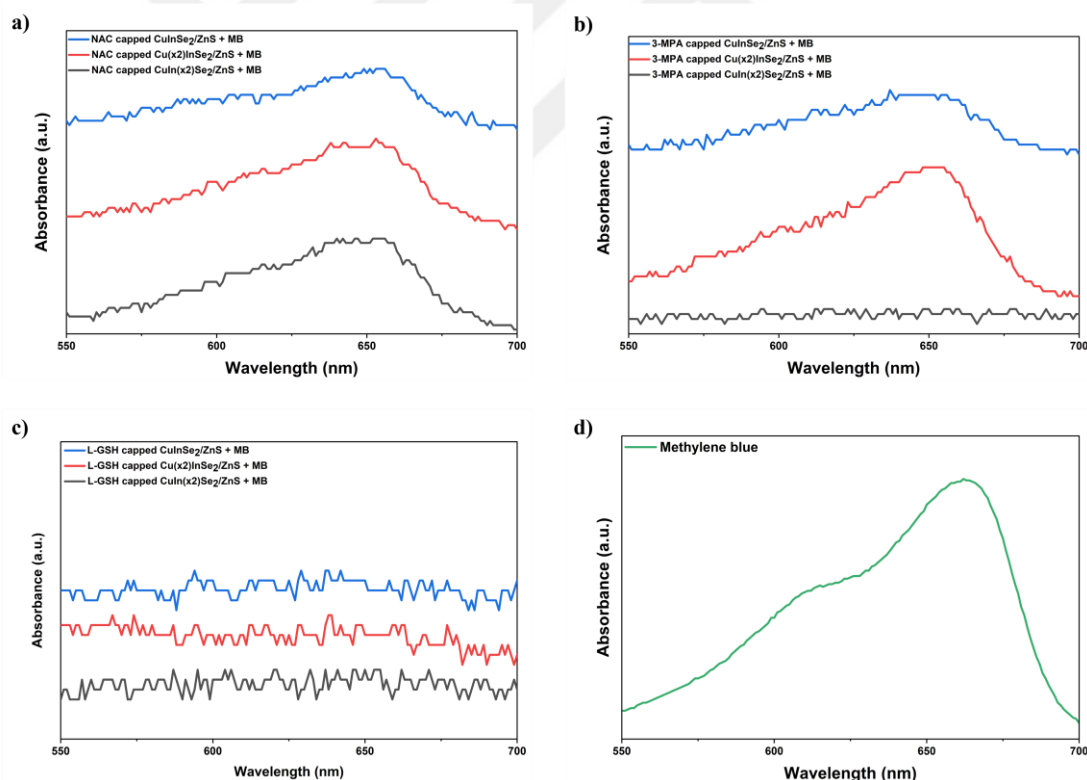


Figure 3.17 : UV-Vis desorption profiles of MB in methanol solvent from a) NAC b) 3-MPA c) L-GSH-capped QDs d) the reference absorption spectrum of pure MB.

The most obvious indication that the dye has been recovered is observation of the characteristic absorption peaks of dye molecules in the UV spectra obtained after desorption study. This indicates that the adsorbed dye molecules have been released

from the surface of the QDs with the use of methanol and have been transferred to the solution. The spectrum shown in Figure 3.17d represents the characteristic absorption peak of MB around 662 nm as a reference. Additionally, the type of ligand is another significant parameter at this point. In particular, the specific absorption peak of MB is observed in all absorbance spectra for desorption studies with all NAC capped QDs. Desorption of MB from 3-MPA capped QDs was observed in samples synthesized using the standard reaction conditions as well as in those prepared with a doubled amount of copper precursor. In those QDs that capped with the L-GSH, desorption with methanol was not observed at all. This may be the result of low initial dye adsorption efficiencies of these QDs and also the bulky nature of L-GSH may facilitate stronger dye-ligand interactions and steric confinement effects, resulting in increased dye retention and hindering desorption. Figure 3.18 shows the UV-Vis spectra obtained from the desorption studies of RB interaction with QDs.

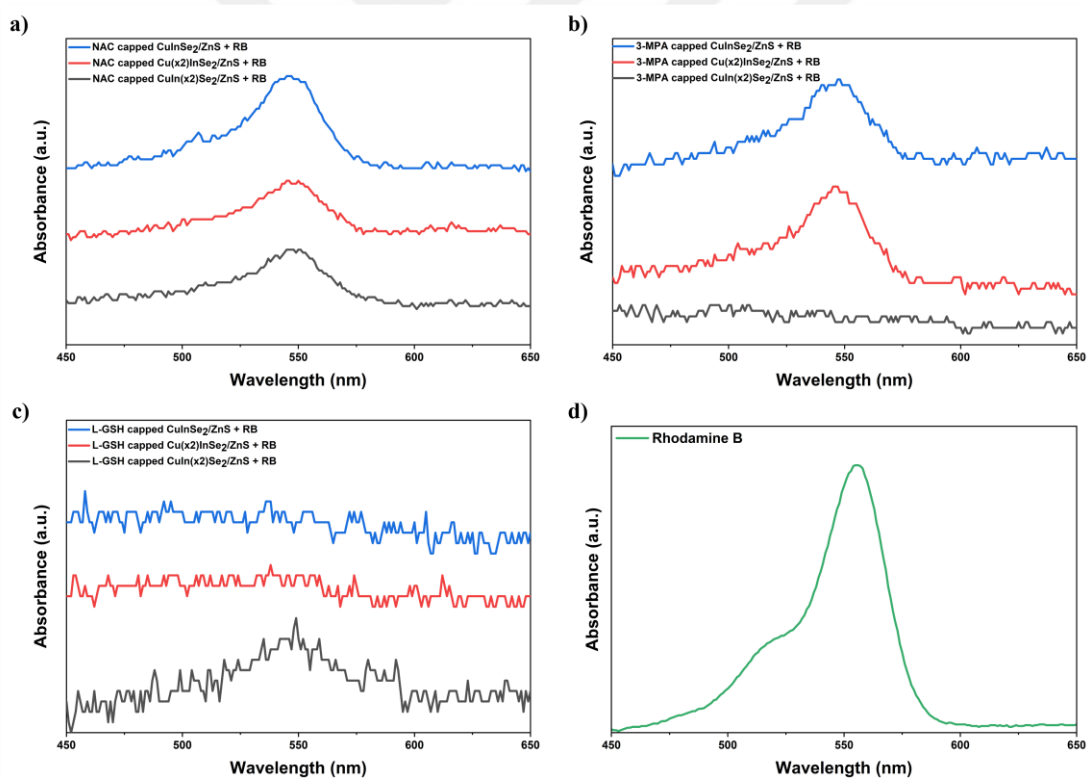


Figure 3.18 : UV-Vis desorption profiles of RB in methanol solvent from a) NAC b) 3-MPA c) L-GSH capped QDs d) the reference absorption spectrum of pure RB.

The absorption peak of pure RB at 556 nm (Figure 3.18d) was clearly observed in the absorbance spectra of desorption studies performed with NAC-capped QDs, indicating that the methanol successfully extracted the dye molecule. For 3-MPA-capped QDs,

although with a doubled amount of indium precursor retained the dye at a rate of 44.8%, as shown in Table 3.1, the desorption of the dye was not observed, indicating the interactions between dye molecule and QD were strong enough to prevent its release. In L-GSH-capped QDs, it was found that desorption efficiency was very insignificant that only the QDs with a doubled amount of indium precursor has resulted with minor release of the dye molecule.

The UV-Vis spectra obtained from the investigation of the desorption behavior of the anionic MO from QDs+MO in methanol was demonstrated in Figure 3.19.

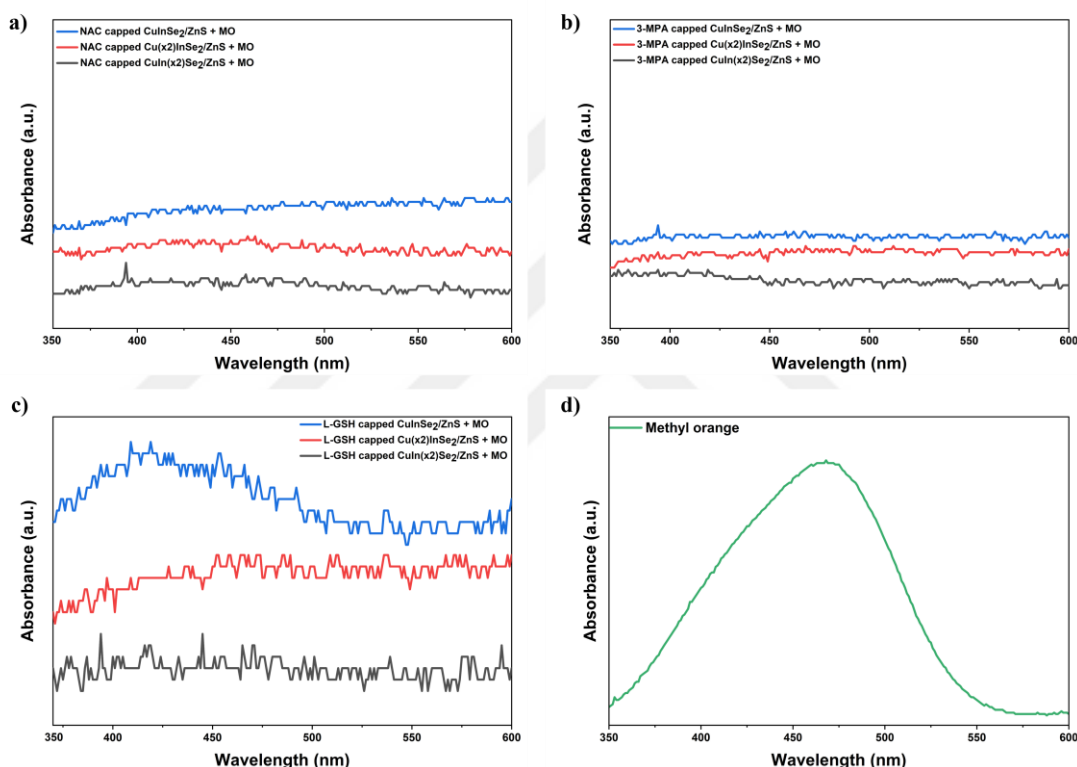


Figure 3.19 : UV-Vis desorption profiles of MO in methanol solvent from a) NAC b) 3-MPA c) L-GSH-capped QDs d) the reference absorption spectrum of pure MO.

In comparison with MB and RB, MO's characteristic absorption peak at 465 nm was not observed nearly for all of the absorbance spectra of desorption studies. This finding is consistent with the adsorption results presented in Table 3.1, which indicate that MO exhibited the lowest adsorption efficiency among the investigated dyes. Consequently, the amount of desorbed MO was likely below the detection level required to generate a distinct absorption peak in the UV-Vis spectra. The adsorption efficiencies in Table 3.1 are clearly compatible with the results obtained here; in particular, the 3-MPA capped $\text{CuIn}(x_2)\text{Se}_2/\text{ZnS}$, which has the lowest adsorption percentage (3-55%),

similarly shows the most linear line in the spectra at zero during desorption in comparison to the others.

In the case for desorption studies with L-GSH and NAC capped QDs + MO, although the adsorption efficiency was around 35-70% the desorption of the dye molecule from the surface of the QDs was very limited. These may be resulted from the strong interaction between these QDs and MO.

The following equation 3.2 was used to calculate the areas under the UV curves plotted in Origin software in order to measure desorption efficiency.

$$\% \text{ Desorption Efficiency} = \frac{A_{des}}{(A_d \times A_{ads})} \times 100 \quad (3.2)$$

In this equation, A_{des} refers to the absorbance value after the desorption process, A_d indicates the absorbance of the pure dye solution, and A_{ads} is the dye removal efficiency value from the adsorption experiment. The results of this calculation are shown numerically in the Table 3.2.

Table 3.2 : The desorption efficiencies of QDs for MB, RB, and MO.

	MB (%)	RB(%)	MO (%)
NAC capped CuInSe ₂ /ZnS	7.9	12	-
NAC capped CuIn(x2)Se ₂ /ZnS	11.4	8.6	-
NAC capped Cu(x2)InSe ₂ /ZnS	11	7.8	-
3-MPA capped CuInSe ₂ /ZnS	6.5	5.8	-
3-MPA capped CuIn(x2)Se ₂ /ZnS	-	-	-
3-MPA capped Cu(x2)InSe ₂ /ZnS	14.4	18.9	-
L-GSH capped CuInSe ₂ /ZnS	-	-	6.2
L-GSH capped CuIn(x2)Se ₂ /ZnS	-	5	-
L-GSH capped Cu(x2)InSe ₂ /ZnS	-	-	-

As a result, both when stated as a percentage and when analyzed using UV-Vis spectroscopy, methanol generally enables dye recovery in desorption processes for NAC- and 3-MPA capped + cationic dyes at the rates specified in Table 3.2; whereas, for MO dye, no peak is expected during desorption due to the relatively low amount of dye adsorbed initially, rather than the method itself. The second method besides methanol involved a thermal-based process of interacting with distilled water, heating it to 50 degree celsius, and stirring it, but no recovery of dyes was observed using this method.

4. CONCLUSION

The synthesis of cadmium free core/shell CuInSe₂/ZnS QDs was successfully carried out in aqueous one pot synthesis method under reflux conditions and nitrogen gas for a total reaction time of 1.5 hours.

The structural characterization of the synthesized QDs was examined using XRD, confirming that the materials are quantum dot and that a core/shell structure has formed. According to the FTIR spectra, all ligands had successfully linked to the QDs via sulfur atoms, which was proved with the disappearance of thiol peaks around 2500 cm⁻¹.

In adsorption experiments conducted with MB, RB and MO dyes, MB exhibited the best interaction with the QDs, and the highest removal efficiency of 99.1% was achieved with NAC capped Cu(x2)InSe₂/ZnS based on the absorbance spectra. Examining the FTIR spectra obtained after dye adsorptions reveals that the adsorption mechanism can be explained with hydrogen bonding and hydrophobic interactions, besides electrostatic interactions.

For the dye recovery, desorption experiments were conducted. While dyes could not be recovered using the thermal based approaches of dispersing them in distilled water at 50 degree celsius in a water bath. Second approach is the use of methanol as a desorption solvent which provided the recovery of dyes, particularly RB and MB, the characteristic absorbance spectra were obtained with UV-vis spectroscopy.

To sum up, due to their high adsorption efficiencies of these CuInSe₂/ZnS QDs to a variety of dyes, they can be used in waste treatment applications.



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